LEACHING BEHAVIOUR, MECHANICAL AND DURABILITY PROPERTIES OF MORTAR CONTAINING MUNICIPAL INCINERATION BOTTOM ASH

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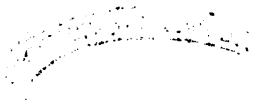


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To a person who taught me how to love people as I would want them to love me, help everyone and be happy irrespective of the circumstances

Angela Hernandez-Acevedo

To my mum, the best mum that I could ever have wished for

you will always be with us

ABSTRACT

The review of municipal solid waste (MSW) management scheme has indicated that the amount of MSW sent to incineration plants will increase in the UK in coming years. Therefore, the amount of municipal solid waste incineration (MSWI) residues generated will increase significantly. MSWI residues are divided into MSWI fly ash (MSWI-FA) and MSWI bottom ash (MSWI-BA). MSWI-FA is classified as hazardous residue thereby requires special treatment before disposal. MSWI-BA is mostly disposed in landfill sites. MSWI-BA fraction with particle size diameter below approximately 2mm has low engineering properties and may have an adverse effect on the environment due to its high porosity, solubility and leachability of possible toxic compounds. This research programme has investigated new potential uses and leaching behaviour of mortar containing MSWI-BA with particle size diameters below 2.36mm.

Fraction of MSWI-BA with particle size diameters (∅) below 2.36 mm (∅<2.36) was divided into different sub-fractions to evaluate their influence on compressive strength of concrete when used as partial replacement of cement or sand. MSWI-BA fraction with ∅<212μm (fine fraction) and 212μm<∅<2.36mm (coarse fraction) used as partial replacement of cement and sand respectively, showed higher compressive strength compared with the other fractions examined. In addition, replacing sand with the coarse fraction of MSWI-BA exhibited similar or higher strength than the reference mix.

Examination of physical and chemical properties of the fine and coarse fractions of MSWI-BA unbound indicated that both fractions had potential to be used as replacement of cement or sand. However, the evaluation of their leaching behaviour suggested that they should be bound in cement-based systems to avoid leaching of potential toxic elements.

Evaluation of physical, mechanical and sulfate resistance properties of mortars containing 15% of the fine fraction of MSWI-BA as a partial replacement of cement and 50% of the coarse fraction as partial replacement of sand indicated potential uses in concrete production.

In addition, the leachability of mortar specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively was significantly reduced when compared to unbound MSWI-BA fractions.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Municipal solid waste (MSW) plays an important role within the management of waste (**1**). Throughout the world, landfilling has been the most popular scheme to dispose of MSW (**2,3**). However, this trend is changing and there is an international action plan to re-use or recycle MSW instead of sending them to landfill sites (**4**). Incineration of MSW seems to be an alternative option. Reduction in volume, energy recovery and cheaper energy costs compared with other recycling methods, are some of the advantages of incineration (**5**). Thus, it has been predicted that the amount of MSW sent to incineration facilities will increase in the coming years (**6,7**).

At present, disposal in an environmentally sound manner the residues that are produced during incineration are the main concern associated with incineration (**4**). Incineration of MSW produces two types of residues; municipal solid waste incineration fly ash (MSWI-FA) and municipal solid waste incineration bottom ash (MSWI-BA). MSWI-FA contains a high content of toxic compounds and it is classified as hazardous waste. MSWI-BA represents approximately 90% of the total amount of MSWI residues generated and rarely needs special safety landfill sites (**5**).

In general, MSWI-BA is disposed of in landfill sites (**8**). However, the utilisation of MSWI-BA in construction is being encouraged to reduce landfill area required and to conserve natural raw materials such as virgin aggregates (**9-12**). MSWI-BA can be used as unbound material (e.g. road base) or in bound material (e.g. partial replacement of aggregates). In the past decades, MSWI-BA ash was used extensively as filling material without being bound with other materials. However, the use of unbound MSWI-BA has been reduced as a result of health and environmental awareness due to the possible leaching of toxic substances to the environment (**8,12,13**).

The performance of MSWI-BA in construction is the key to its successful utilisation. Performance of MSWI-BA as a construction material depends largely on its physical and chemical properties, which can vary broadly even for the same incineration facility. MSWI-BA commonly exhibits high susceptibility to freeze and thaw as a result of its high porosity and tendency to absorb water (**14**). Freeze and thaw susceptibility can be enhanced significantly if fine grains (e.g. particles with diameters below 3mm or 2mm) are removed from the whole MSWI-BA stream (**14,15**). In addition, the chemical characterisation of MSWI-BA suggests that fine particles may contain higher contents of toxic compounds (e.g. heavy metals, sulfates) than coarser particles (**14**).

Therefore, having identified the need to find uses for the fine fraction of MSWI-BA and the environmental concert on using MSWI-BA as unbound material, this programme of research was set up to investigate potential utilisation of fine fractions of MSWI-BA bound in cement-based systems.

1.2 AIMS AND OBJECTIVES

The aims of the research programme are to examine the performance of MSWI-BA in the production of concrete and to assess the environmental impact of concrete containing MSWI-BA. In order to achieve these aims, the objectives of the current programme of research are to;

1. Examine the physical and chemical properties of unbound MSWI-BA.
2. Evaluate leaching behaviour of unbound MSWI-BA.
3. Determine the compressive strength of mortar containing different fractions of MSWI-BA used as a partial replacement of cement or sand.
4. Evaluate the physical and mechanical properties of mortar containing MSWI-BA as a partial replacement of cement and sand. These properties include drying shrinkage, porosity and mechanical compressive strength.
5. Assess the sulfates resistance of mortar containing MSWI-BA as a partial replacement of cement and sand.
6. To evaluate the leaching behaviour of MSWI-BA bound in cement-based systems.
7. To examine the relationship between physical, mechanical durability properties and leaching behaviour of mortars containing MSWI-BA.

1.3 EXPERIMENTAL PROGRAMME

Figure 1.1 shows the experimental programme that was conducted to achieve the objectives of this research. Having collected MSWI-BA from an incineration plant and carried out an appropriated sample reduction, different particle sizes of MSWI-BA were subjected to characterisation. The characterisation included the examination of physical, chemical and environmental properties of different fractions of MSWI-BA (**Chapters 4** and **5**). In parallel, the compressive strength of mortars containing MSWI-BA as a partial replacement of cement or sand was examined. Compressive Strength was determined for different particle sizes of MSWI-BA. As a result of the compressive strength evaluation, the fractions of MSWI-BA with diameter below 212μm and the fraction with diameter ranging from 212μm to 2.36mm were chosen to replace cement and aggregate respectively.

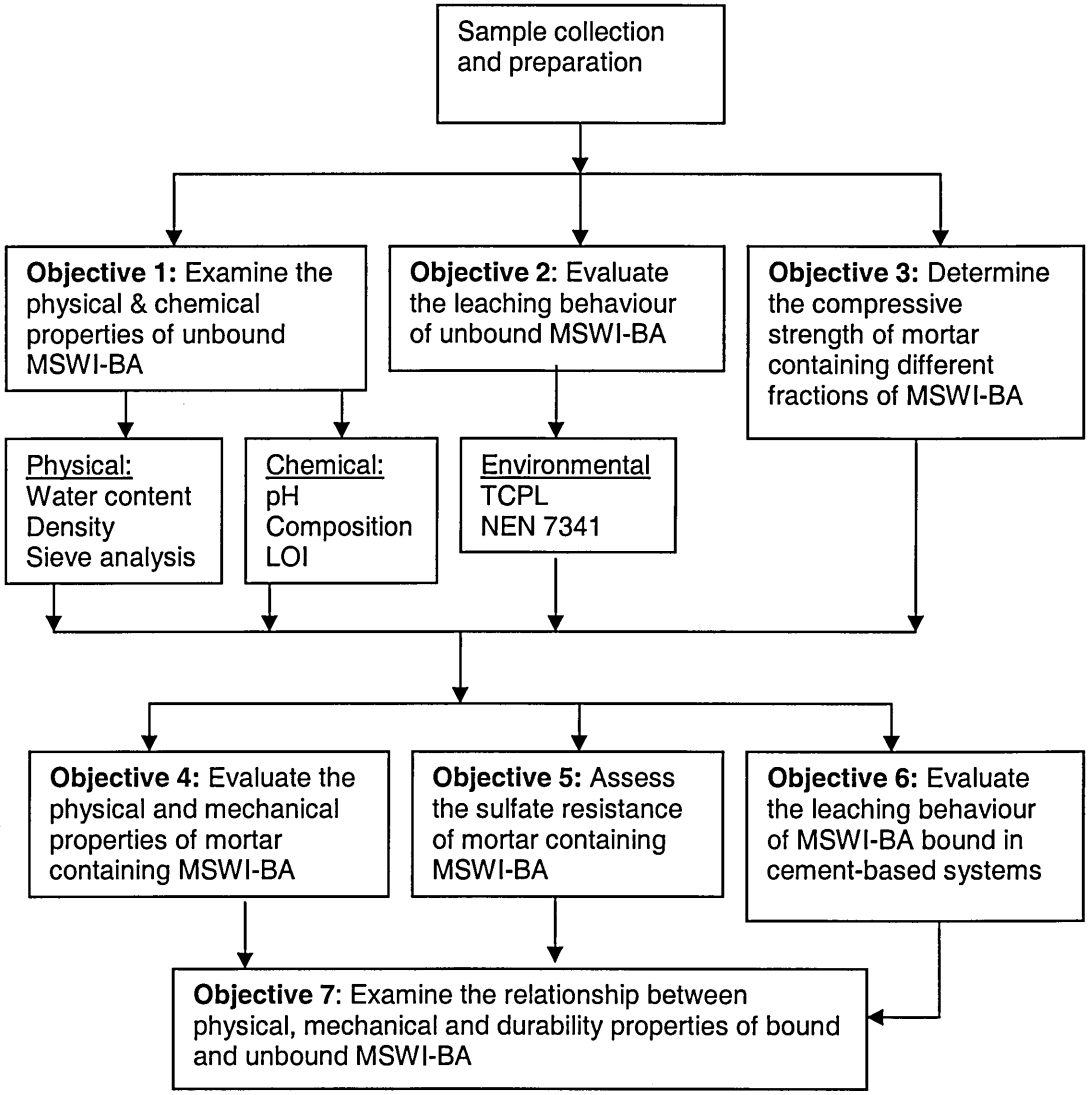


Figure 1.1. Experimental Programme

Having decided to use MSWI-BA as a partial replacement of cement and aggregates, the influence of using different replacement levels of MSWI-BA on physical, mechanical and sulfate resistance properties was evaluated. Physical and mechanical properties of mortar containing MSWI-BA are presented in **Chapter 6**, whereas sulfate resistance is evaluated in **Chapter 7**. **Chapter 8** examines the leaching behaviour of mortars containing MSWI-BA. In Chapter 8, mortar containing MSWI-BA was examined under different leaching conditions, in order to simulate different leaching scenarios. Final conclusions, limitations and future recommendations of this programme of research are also drawn in **Chapter 9**.

1.4 SCOPE OF THE PRESENT INVESTIGATION

The current thesis has been divided into nine chapters, whose contents are summarised as follows;

This chapter, **Chapter 1: "Introduction"** gives an overview of the topic investigated including the aims, objectives and experimental plan of the research programme. In addition, a summary of each chapter is introduced.

Chapter 2: "Literature Review" includes a-state-of-the-art of the role of municipal solid waste incineration (MSWI), the physical and chemical properties and current utilisation of MSWI-BA. The review suggests an increase in the quantity of MSW sent to incineration plants, and therefore an increase in MSWI-BA generated. The examination of physical and chemical properties of MSWI identifies potential uses of MSWI-BA in cement based systems.

In addition, chapter 2 reviews the chemistry of cement, physical, mechanical and durability properties of cement-based systems. The study of chemistry provides a summary of main components and reactions that control the hydration and hardening properties of plain and composite cement-based systems. Hence, pore water composition, alkali-silica reaction and the effect of metals, sulfates and chlorides on cement hydration and formation of hydrates, are some of aspects examined.

Finally, chapter 2 examines the effects of using waste materials in cement-based systems on compressive strength, drying shrinkage, porosity, sulfate resistance and leaching behaviour of such systems.

Chapter 3 "Materials, Techniques and Test Methods" provides a description of materials, instruments and techniques used throughout the experimentation programme. Apart from the theoretical background given for the main techniques used, testing and the optimisation of testing are also described. In addition, common methodology employed throughout the experimental chapters is provided. Specific methods that were used for particular tests are given in the relevant chapters.

Chapter 4: "Physical and Chemical Properties of Unbound MSWI-BA" includes the determination of water content, bulk and particle densities, grading analysis, pH, inorganic composition and LOI for different fractions of MSWI-BA. The different fractions of MSWI-BA were:

- Fraction 1 consisted of a raw fraction that contained particles with diameter (∅) below 10mm and coded as Raw BA ∅<10mm. Particles of the raw fraction with ∅>10mm were removed manually).
- Fraction 2 consisted of particles with ∅<212μm and referred as ∅<212μm.
- Fraction 3 contained particles with 212μm∅<2.36mm and referred as 212μm<∅<2.36mm.

- Fraction 4 consisted originally of particles with diameter below 2.36mm that were ground for 3 minutes using a hammer mill. After grinding, the diameter of particles was below 150μm. Fraction 4 was coded as ground MSWI-BA.

The evaluation of physical and chemical properties of MSWI-BA contributed to the present knowledge about MSWI-BA characteristics, and the discussion of MSWI-BA behaviour in concrete.

Chapter 5: "Leaching Behaviour of Unbound MSWI-BA" examines the leaching behaviour of different fractions of MSWI-BA in order to determine the presence of toxic elements and maximum concentrations of metals that can be leached out. Two leaching procedures were conducted; the toxicity characteristic leaching procedure (TCLP) (**16**) and NEN 7341 (**17**). The fractions of MSWI-BA tested for both leaching procedures were fractions 2, 3 and 4 (∅<212μm, 212μm<∅<2.36mm and ground BA). The leaching behaviour of MSWI-BA included the determination of twenty-two elements. Within the 22 elements, a group of toxic elements (e.g. Ni, Cr, Sn, Mo, As, Se, Hg, Cd, Co) were analysed together with other elements of interest such as Ca, Si, K, Na, Al, Fe, Mg, Ba, Cu, Zn, B, Mn and Pb.

Chapter 6: "Physical and Mechanical Properties of Mortar Containing MSWI-BA" evaluates the influence of MSWI-BA as partial replacement of cement and sand on physical and mechanical properties of mortars. The properties were saturated density, porosity, drying shrinkage, compressive and flexural strengths. The compressive strength results were used as key parameters to select the fractions of MSWI-BA that partially replaced the cement or sand in other chapters (e.g. sulfate resistance and leaching behaviour). Within the different MSWI-BA particle sizes subjected to compressive strength testing, fractions 2 and 3 (∅<212μm and 212μm<∅<2.36mm) were selected to partially replace cement and sand respectively. In addition, the fraction with ∅<300μm was also used as partial replacement of cement in the drying shrinkage testing.

Chapter 7: "Sulfate Resistance of Mortar Containing MSWI-BA" assesses the sulfate attack of mortars containing different amounts of MSWI-BA as a partial replacement of cement and sand. The levels of sand replacement by MSWI-BA fraction 3 (212μm<∅<2.36mm) were 0, 25 and 50%, whereas cement was replaced by 0, 15, 20, 30% of MSWI-BA fraction 2 (∅<212μm). Sulfate attack procedure consisted of placing mortar in 5% (by weight) sulfate solutions that were renewed monthly. Sulfate attack was evaluated by measuring change in weight, length, strength and visual observation during approximately 600 days exposed to sulfate solution.

Chapter 8: "Leaching Behaviour of Mortar Containing Bound MSWI-BA" includes the determination of metals, chlorides and sulfates in leachates from mortar specimens containing MSWI-BA. The metals analysed were Ca, Si, K, Na, Al, Mg, Zn, Cu, Pb, Cr, Ba, Hg, Ni, Cd, As, B, Mn, Sn, Sb, Mo and Co. Tank procedure was chosen as leaching method to obtain the leachates from mortar specimens. The leachant removal times, test duration and solid/leachant ratio were used in accordance with NEN 7345 (**18**). These experimental parameters were constant for all different leaching procedures that were carried out. The leaching behaviour of mortars containing MSWI-BA was conducted to evaluate the binding capacity of cement-based systems and to assess the effects of heavy metals, sulfates and chlorides on the cement-based system properties.

Chapter 9: "Conclusions, Limitations and Future Recommendations" summarises the conclusions and defines the limitations and future recommendations related to the use of MSWI-BA as a construction material.

1.5 REFERENCES

1 Environmental Agency. "Waste Minimisation and the Environmental Agency". DO40APRLR. 1999

2 Sawell S.E., Hetherington S.A. and Chandler A.J. "An Overview of Municipal Solid Waste Management in Canada". Waste Management, Vol 16, Nos 5/6, pp 351-359. 1996

3 EPA "International Solid Waste Practices". Review 1997 Http://www.epa.gov/epaoswer/non-hw/muncpl/factbook/internet. Visited 19 Feb.2002

4 Sakai, Sawell S.E. and Chandler A.J. "World Trends in Municipal Solid Waste Management". Waste Management, Vol 16, Nos 5/6, pp 341-350. 1996

5 Péra J. and Ambroise J. "Incineration of Wastes and the Environment". Proceedings of the International Symposium of Sustainable Construction: Use of Incinerator Ash. Edited by R. K Dhir Tom D. Dyer and K. and Kevin A. Paine. Dundee (UK). 2000

6 Author: Ian Jones 20-nov-2001. http://www.environment-agency.gov.uk/news/202518?lang=_e&region=&projectstatus=&theme=&subject=&searchfor=municipal+solid+waste&topic=&area=&month= 19 February 2002

7 Author: Ian Jones -Dec-2001 http://www.environment-agency.gov.uk/news/214030?lang=_e&region=&projectstatus=&theme=&subject=&searchfor=municipal+solid+waste&topic=&area=&month= 19 February 2002

8 Johnson C.A. "A Geochemical Perspective on the Factors that Control Long-Term Emission from Municipal Solid Waste Incinerator". Proceedings of International Symposium "Use of Incinerator ash". Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

9 Westiner E. M.and Löcherer Th. Wörner. "Volume Stability of Hydraulic Bound MSWI Ash." Proceedings of International Symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

10 Wainwright P.J., J.R. Barton and Cresswell D.J.F. "The Long-Term Performance of Untreated Bottom Ash, and the Production and Use of a Lightweight Synthetic Aggregate from the Bottom Ash Fine Fraction." Proceedings of International Symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

11 Paine K.A., Dhir R. K.and Doran V.P.A. "Unprocessed and Processed Incinerator Ash as a Cement Bound Material."Proceedings of International Symposium: Use of Incinerator Ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

12 Frantz G.C. and Demars K.R. "Ash Reutilization Research at the University of Connecticut". Proceedings of International symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

13 Karpinski S., Zhang X., Gress D., Eighmy T. and Janoo V. "A Physical Evaluation of Municipal Solid Waste Grate Ash as an Aggregate Substitute in Alphatic Concrete." Proceedings of International symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

14 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste Incinerator Residues". Studies in Environmental Science 67. Elsevier. Chapter 9. "Bottom Ash". Elsevier 1997

15 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste Incinerator Residues". Studies in Environmental Science 67. Elsevier. Chapter 7. "Characterisation Methodologies". 1997

16 EPA. Toxicity Characterist leaching Procedure Method 1311. July 1992

17 NEN 7341 02.95: "Leaching Characteristics of Solid Earthy and Stony Building and Waste materials. Leaching Test. Determination of the leaching availability of Inorganic Compounds

18 NEN 7345 03. 95.: Leaching Characteristics of Solid Earthy and Stony Building and Waste materials. Determination of the Leaching behaviour of Inorganic Components from Building Monolithic Waste Materials with the Diffusion Test

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

The challenge of encouraging a sustainable waste generation has been adopted over the world and especially by industrialised countries. The principles of any sustainable waste management scheme consist of minimisation, recycling and reuse of waste (**1**). Municipal solid waste (MSW) plays a key role within a general waste management strategy because of its continuous generation and variable chemical compositions and physical characteristics (**1**).

An MSW strategy requires the consideration of a large number of factors such as population density, transportation, socio-economic aspects and environmental regulations (**2**). Therefore, every country or region needs to assess its own requirements in order to achieve the most effective MSW management scheme.

The minimisation of MSW depends widely on the public's attitude towards consumption (**1**). In order to encourage the minimisation approach, improvement of product quality, durability of products and environmental friendliness are being emphasised by Media and Authorities.

Most developed countries are limiting the amount of MSW sent to landfill sites. Landfill should be only used when other options are not available. The major problems associated with MSW landfill sites are space requirements, public concern, land and water contamination and the environmental risk for future generations (**3**,**4**).

Material and energy recovery schemes include re-use, recycle, compost and incineration. Although all these strategies reduce the amount of waste sent to landfill sites, the remaining waste produced requires further handling, transporting and disposal operations.

Since re-use and recycling require separation of waste prior to processing, most developed countries have implemented a separation collection scheme of MSW. Recycling paper and glass waste is already underway and this has recently been extended to plastics and metals. However, many recycling/re-use schemes have not been implemented extensively due to their low economic viability. High manufacturing costs (e.g. energy consumption) and poor public acceptance are some of the factors that reduce commercialisation of recycled materials (**3**).

Composting and other biological technologies of MSW have recently become commercially viable options. The organic material fraction has to be separated from the

MSW and consequently the benefits of implementing must be examined in each particular case.

Table 2.1 provides data on the MSW management scheme in most industrialised countries (**4**). Data are presented as a percentage of the total quantity of MSW generated by each country. In general, most of the countries have adopted landfill sites as the traditional method for managing MSW. Incineration is the second most popular strategy and is mainly used in countries where there is high population density in selected areas such as Japan Switzerland, Netherlands and Germany. In countries (e.g. Canada) with low-density population, they have used dumping of MSW in landfill sites as the most popular strategy. In addition, the United Kingdom was the country that used landfill most extensively compared with other countries examined.

Table 2.1. MSW Managing schemes in the industrialised countries (Warmer Bulletin, (4)

	Landfill (%)	Recycling (%)	Incineration (%)	Composting (%)
Canada	81.00	10.00	9.00	0.00
France	45.00	3.00	42.00	10.00
Germany	42.00	16.00	40.00	2.00
Italy	77.50	3.00	12.50	7.00
Japan	14.50	20.00	62.50	3.00
Netherlands	41.00	16.00	38.00	5.00
Spain	65.00	13.50	4.50	17.00
Sweden	29.00	20.00	48.00	3.00
Switzerland	11.00	22.00	60.00	7.00
United Kingdom	89.00	2.00	9.00	0.00
United States	58.50	23.00	15.00	3.50

Incineration of MSW has been used extensively in countries where the population density is high and the availability of landfill space is limited. The main objectives of incineration are the reduction of waste volume (up to 90% reduction) and sterilisation of waste (**2**). In addition, most of the modern incinerator facilities are now designed to recover a substantial portion of energy inherent in the waste, thereby producing electricity and/or heat (**5**). Despite these advantages, the practice of MSW incineration has always been subjected to continued public opposition. This is due to the toxic emission of gases and disposal of residues (e.g. ash) produced by the incineration (**1**,**2**,**6**).

Although incineration reduces the weight of waste dramatically, however between 20% and 30% of the original weight is still left as ash (**2**). The total ash discharged from incinerators is usually separated in two parts; Municipal Solid Waste Incineration Fly Ash (MSWI-FA) and Municipal Solid Waste Incineration Bottom Ash (MSWI-BA). In Europe, both parts are classified and managed differently due to the significant differences in their physical and chemical characteristics. The fly ash part contains high concentration of heavy metals and organic pollutants such as polychlorodibenzeno-dioxins and furans. Fly ash requires special safe landfill conditions, whereas bottom ash can be disposed of in landfill without special requirements. Furthermore, in many countries, a processed bottom ash is permitted to be used in construction when its environmental performance has been tested and does not affect human health and the environment.

2.2 MUNICIPAL SOLID WASTE INCINERATION

The support of burning MSW is continually increasing in countries where population is concentrated in narrow areas, because incineration does not require a pre-separation of MSW stream or high transport costs.

Incineration of MSW has three distinctive objectives (**5**):

a) A volume reduction of about 90% and weight reduction of approximately 70%.

b) Stabilisation of waste and destruction of pathogens by the oxidation of the organic compounds.

c) Recovery of energy.

There is a need to evaluate the volume and composition of MSW in any particular region or country before any waste management strategy may be developed. Figure 2.1 shows the generation of MSW per capita per day in major industrialised countries. It can be seen that the United States and Canada produce the highest generation of MSW of the countries examined. The production of MSW for the remaining countries is similar.

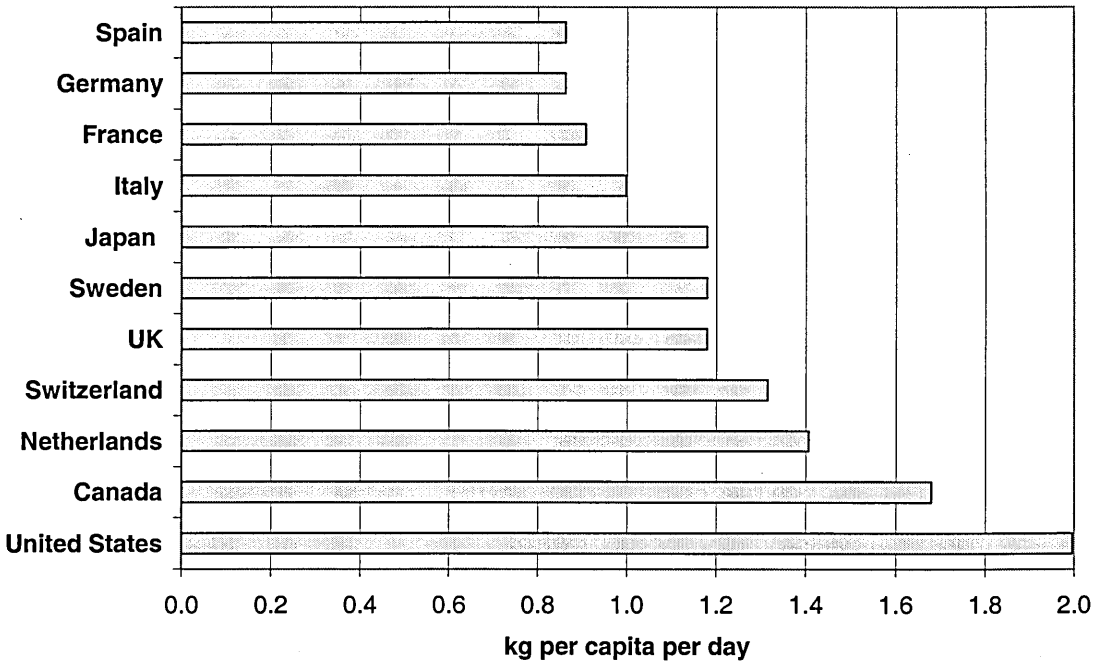


Figure 2.1 Generation of MSW in some developed countries (Warmer Bulletin, (4))

In the United Kingdom the annual generation of MSW has been estimated between 15 and 20 million tonnes respectively (**6**).

2.2.1 Composition of Municipal Solid Waste

Municipal solid waste is considered non-hazardous waste. This waste consists of household and commercial waste. The former includes residential homes, educational establishments and part of the hospital waste. Commercial waste includes waste from shops, offices, businesses and places of entertainment. In general, the major constituents contained in MSW are paper, garden waste, organic waste, metals, plastics and glass (**6**). In addition, MSW contains others constituents such as PVC plastic and batteries which increase significantly the concentration of toxic compounds (**2**).

Figure 2.2 provides the percentage by volume of materials that can be found in an average bin of household waste (**6**). The figure shows that paper, card and organic material are the major constituents representing approximately 50% of the total composition. The other constituents (e.g. plastic, glass, metals) vary from 2 to 10%.

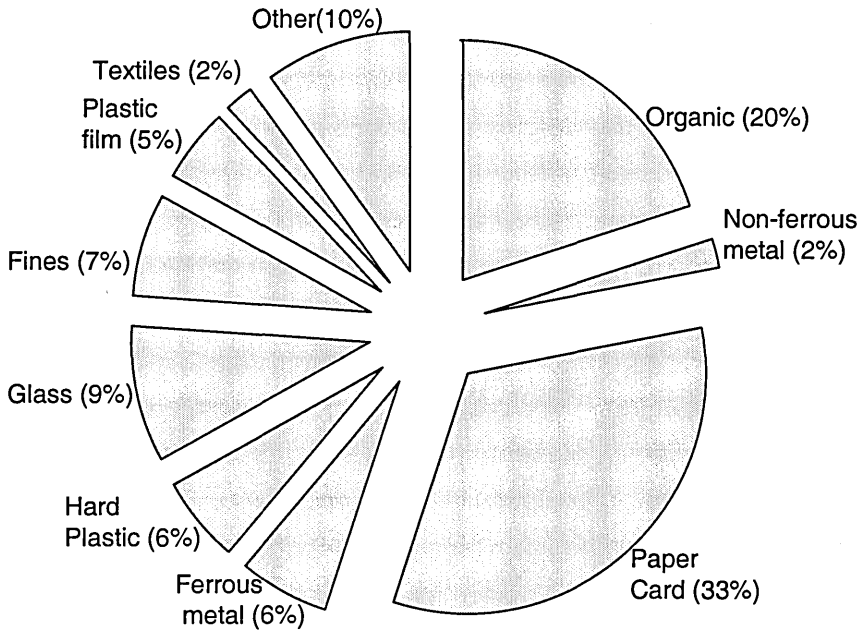


Figure 2.2. Percentage of materials contains in a typical bin stream (Environmental Agency (6))

Paper, textiles and plastics are the most combustible fraction of MSW, and their heating values are 15.8, 32.8 and 18.7 MJ/kg respectively (**7**). It is estimated that one tonne of municipal solid waste has a typical energy content of 12.9 MJ/kg, approximately equal to one third of a tonne of coal (**8**).

2.2.2 Incineration Process

Incineration is defined as the thermal process of MSW by chemical oxidation with excess amounts of air. Basically, incineration plants burn MSW in a furnace that operates at temperatures between 850^{0}C and 1250^{0}C (**9**). The energy content of gases produced during combustion can be used to generate steam to drive a turbine, thereby producing electricity and/or heat. In accordance with emission regulations, municipal solid waste incineration (MSWI) plants have a sophisticated gas cleaning systems to control the release of harmful gases into the atmosphere. In addition, almost all the modern facilities have magnetic extraction systems to recover ferrous metals from bottom ash. The output products coming from incineration facilities include a hot stream of gases, mainly N, CO_2 and H_2O and non-combustible residues, knows as ashes. The mass balance of a common incineration plant with energy recovery is presented in Table 2.2 (**10**).

Table 2.2. Mass balance of a MSWI facility (Tyseley Waste Plant (10))

IN	OUT
100 tonnes of MSW	35.5 tonnes of steam
833kg of lime (to control pH)	17 tonnes of bottom ash
36kg of ammonia (to control NOx emissions)	3 tonnes of fly ash
21kg of activated carbon (to control Hg emissions)	3 tonnes of scrap metal.

Figure 2.3 shows a sketch of an incineration plant that recovers energy from waste (**11**). The mixed garbage is lifted into the feed and moves down the grate, known as primary combustion zone, where it is burned. Incombustible material drops to the ash quenching tank while combustible and fine materials go to the waterwall furnace. The coarse combustible material that can not get to the top of the furnace, drops to the ash quenching tank. Gases and finer particles pass to the superheated and then to the economiser. The heat recovery from the waterwall furnace is superheated providing enough steam to drive a turbine. Gases and dust pass to the emission control system, which is designed to condense heavy metal and neutralise the acid gases and remove fly ash particles.

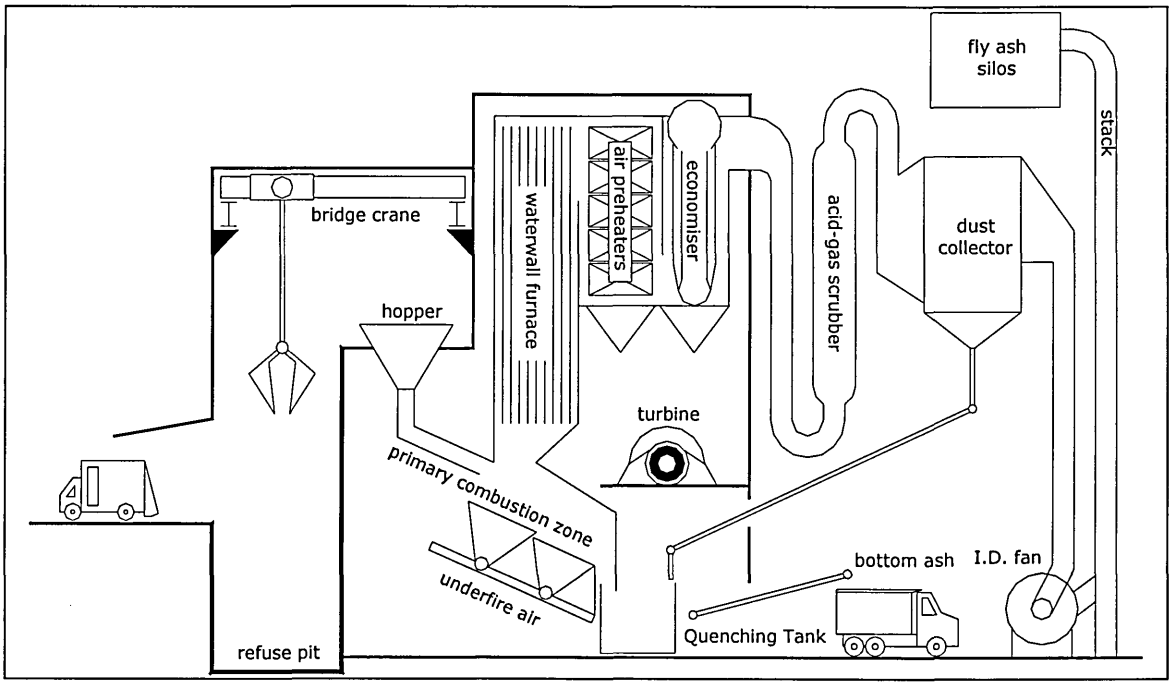


Figure 2.3. Sketch of an incineration plant with energy recovery (11)

In the cleaning systems, the flue gas is cooled by injecting atomised water droplets and then heavy metals are condensed. Next, dry hydrated lime is injected into the gas to react with acid gases, forming solid products including $CaSO_3$ and $CaCl_2$. Some new incinerators inject ammonia and carbon to control NO_x and mercury emissions respectively (**4**). Solid products pass to filters where they are removed. Finally, cleaned flue gas is discharged through the stack and the dust is collected by fly ash silos.

2.2.3 Municipal Solid Waste Incineration Residues

Commonly, the MSWI residues are divided into two parts; MSWI-FA and MSWI-BA. MSWI-BA includes coarse material and is approximately 90% of the total MSWI residues generated (**7**). Generally, MSWI-BA includes grate sifting materials and non-combustible materials, known as grate ash. Physical, chemical and leaching characteristics and potential utilisation of bottom ash is discussed in more detail in 2.3.

MSWI-FA includes the finer particles and the precipitated solids of the gas cleaning systems. The common mineral phases found in fly ash are CaClOH, $Ca(OH)_2$, $CaSO_4$, NaCl, KCl, SiO_2, $CaCO_3$, CaO and Al_2O_3. In addition, fly ash contains heavy metals such as Pb, Zn, Ba, Cd, and Sr (**12**). MSWI-FA is considered to be a toxic waste due to its potential risk to health and the environment. Therefore, safety in incineration plants, transportation and disposal of MSWI-FA require an adequate assessment. Several stabilisation techniques such as melting-solidification, cementing-solidification, chemical stabilisation and acid extraction are being used to reduce the risk of fly ash in landfill sites. Chemical composition, environmental impacts, disposal techniques and further application of fly ash have been discussed widely elsewhere (**12- 16**).

2.2.4 Environmental Concern and Future of Incineration

Since the first incinerators were built in order to reduce the amount of MSW sent to landfill sites, there have been considerable concerns over the emission of hazardous substances into the atmosphere and the generation of residues that need further treatment and/or disposal.

Stringent regulations (**17**) were established to reduce toxic emission including dioxins, furans and airborne. As a result, incineration techniques have improved through better design, operation and air pollution control systems to the point where emissions are no longer considered a risk to human health and the environment (**18**).

Moreover, incineration is not free of residues; approximately 30% by weight of the total amount of MSW ends up as ashes (MSWI-FA and MSWI-BA). The incineration

residues are usually disposed of in landfill sites. However, investigation on potential utilisation of fly ash and bottom ash is being conducted extensively to enhance their uses and to reduce landfill tax and environmental impact on the environment (**19**).

Incineration plants are expensive to implement, run and maintain. They require long-term contracts with local councils to guarantee a steady supply of MSW (**20**). Incineration practices seem to encourage waste production rather than minimisation due to the long contract required, which may be prolonged up to 25 years in most cases. Despite the emphasis on waste minimisation, it is recognised that society will carry on generating wastes that require incineration in the future (**18**). Hence, in the UK there is an expected increase in the quantity of MSW incinerated from 4.1 million tonnes by 2000 to 7.7 million tonnes by 2005 (**8**). Evidence of that trend was reported by Sir John Harman (Environment Agency Chairman) on 21st of November and 6th of December the of 2001 (**21,22**): household waste is growing by around three per cent each year. If growth continues at that rate, we will need nearly twice as much waste disposal capacity by 2020 as we would if waste production remains at current levels. We must re-use more, re-cycle more, compost more and recover more energy from waste. Furthermore, it was also reported that "there are currently 15 municipal waste incinerators operating in the UK. Estimations show that could be around 100 over the next 10 years".

The factors that will increase the application of incineration and reduce the environmental concerns are as follows:

1. increase in Landfill Tax,
2. reduction of landfill sites,
3. development of energy recovery technology,
4. lower transport and energy costs than other recycling schemes,
5. increase in stringent regulations to reduce toxic emissions,
6. enhancement to manage MSWI residues in an environmentally sound manner.

2.3 MUNICIPAL SOLID WASTE INCINERATION BOTTOM ASH (MSWI-BA)

Municipal solid waste incineration bottom ash (MSWI-BA) contains approximately 50% of materials which have not changed during combustion (e.g. ceramics, glass, ferrous metals, sand, stones (**23**). The MSWI-BA consists mainly of silicates, oxides, carbonates, amorphous glass phases, several iron minerals and feldspars. In addition,

trace elements (e.g. Zn, Pb, Cu, Cr, Hg) and a variety of sulfates have been identified (**24**).

The utilisation of MSWI-BA, mainly as filling material, was stimulated in most of the European Union countries, Japan and the United States in the last decade (**25,26**). However, its uses have been limited due to the lack of information about its long-term environmental behaviour (**19**). The utilisation of MSWI bottom ash requires knowledge of its intrinsic properties including physical, chemical and leaching properties. To fully characterise MSWI-BA is not easy mainly due to the wide number of factors influencing ash characteristics, including:

1. Changing nature of the MSW.
2. Different incineration technologies and operation conditions applied. Temperature is a significant factor to take into account in MSW incineration. Temperatures over 900ºC reduce the release of dioxins and furans in the flue gas steam and also the concentration of toxic compounds in MSWI-BA (**7**).
3. Variety of components forming the bottom ash. A sampling strategy is considered an important factor within the characterisation of MSWI-BA.
4. Poor state of knowledge to assess long-term environmental behaviour (**19,27**).

In order to achieve an indication of physical, chemical and environmental, characteristics of MSWI-BA, it is recommended (**18**) that the following parameter are evaluated:

a) Physical testing includes visual observation, particle size distribution, density, moisture content, absorption capacity, durability, permeability and strength development.

b) Chemical and environmental testing includes loss on ignition, pH, acid neutralisation capacity, elemental and mineralogical compositions, chemical speciation, solubility, presence of complexing agents.

2.3.1 Physical Properties

In most of the incineration facilities, MSWI-BA is processed prior to subsequent disposal. This pre-treatment process can entail quenching, size separation and storage at the incineration plant. The quenching stage is conducted to cool the ash and reduce dust emission. The separation stage always produces a reject fraction which often comprises of ferrous and non-ferrous materials, large pieces of construction debris and unburned materials (**26**). The proportion of the reject fraction depends on waste input and future uses. In Europe a cut off size between 40 mm and 50mm is often used. In

general, MSWI-BA fraction with diameter higher than 40-50mm contains enough ferrous to have an economic value (**28**).

2.3.1.1 Water Content

Water content expressed as moisture content identifies the mass of free water, which is an important parameter with respect to transportation, storage and processing for either disposal or utilisation of MSWI-BA. High water content increases leaching reactions in landfill sites and makes compaction and handling difficult. In addition, water quenching caused the hydration of any cementitious phases present in the MSWi-BA and cementitious properties will be lost. On the other hand, lack of water in the MSWI-BA causes a huge amount of dust. It is estimated that MSWI-BA requires a minimum of 17% moisture to prevent dust emission (**29**).

Water content is controlled for utilisation of MSWI-BA as granular fill applications, road sub-base applications or asphalt paving applications. Water contents of MSWI-BA can be expressed as a percentage of the weight of the water divided by the weight of dry material or the weight of the water divided by the total weight of wet material. Water contents between 25 % and 45% are commonly reported for MSWI-BA (**30-32**). Water content is mainly affected by the quenching stage at the incineration facility, the possible evaporation and leaking of water during handling.

2.3.1.2 Absorption

The determination of absorption capacity of materials is conducted to examine possible changes in weight of materials due to the absorption of water into permeable pore spaces within particles. Absorption tests are widely used in evaluating properties of granular material. However, absorption tests are not suitable for materials that are soluble in water and contain a great proportion of fine grains.

It is well known that MSWI-BA is highly porous and has a tendency of absorbing water easily (**28**). Therefore, it can also be predicted that MSWI-BA has greater susceptibility to freeze-thaw weathering.

2.3.1.3 Density

Density is used to evaluate homogeneity, porosity and degree of compaction of materials. Therefore, it is an important parameter in evaluating the civil engineering properties of MSWI-BA. Density of materials can be expressed using different concepts, including:

a) Bulk density which is the mass of a material that would fill a container of unit volume. It is usually expressed as dry density which is defined by the weight of material divided by its original volume before drying. Bulk density can be used for either un-compacted (loose) or compacted materials. The bulk density depends on the intrinsic density of all particles and the characteristics of materials such as grain distribution and shape of particles (**33**), which determine the potential degree of packing achieved.

b) Specific gravity which is defined as the ratio of the weight of a given volume of sample to the weight of an equal volume of water both at a standard temperature and pressure (**33**). Depending upon the volume of particle included, there are several types of specific gravity; the absolute specific gravity that excludes the volume of permeable and impermeable pores; the apparent specific gravity that includes the volume of impermeable pores but not the capillary ones; and gross apparent specific gravity that includes all the volume of permeable and impermeable pores.

Thus, the difference between bulk density and absolute specific gravity is that the former includes the volume of voids within particles and the latter always excludes this volume. It has been reported that for MSWI-BA with a diameter below 4.75mm, the gross specific gravity varies between 2.31 and 2.56 (**29**), whereas, for natural aggregates the specific gravity ranges between 2.4 and 3.0 (**33**).

2.3.1.4 Particle Size Distribution

Particle size distribution is used to assess the physical properties of materials, this includes for example permeability and frost susceptibility. A uniform gradation means that there are similar proportions of particles within the different ranges of sizes. This indicates potential use of the material as an aggregate substitute. In general, well-graded materials tend to be resistant to erosion and can be readily compacted to a dense state (**28**). Table 2.3 shows the grading of natural aggregates used for concrete (**34**) and for a typical MSWI-BA (**35**).

Furthermore, it has been reported (**26,28-32**) that the use of fines of the MSWI-BA may cause problems (e.g. susceptibility to freeze-thaw) in civil engineering applications due to the high tendency of this fraction to absorb water and its low specific gravity. Thus, in some processing facilities, fines are being removed from bottom ash prior to utilisation in order to enhance the properties of MSWI-BA. The fine fraction of MSWI-BA may be sent to landfill sites or divided into fractions.

Table 2.3: Grading of MSWI-BA and Fine Aggregates for Concrete (34,35)

Sieve Size	Bottom ash (%)	Aggregates for concrete			
		Overall limits (%)	Additional limits (%)		
			C	M	F
10 mm	55-100	100	-	-	-
5 mm	30-55	89-100	-	-	-
2.36 mm	20-30	60-100	60-100	65-100	80-100
1.18 mm	18-20	30-100	30-90	45-100	70-100
600 μm	6-18	15-100	15-54	25-80	55-100
300 μm	6-10	5-70	5-40	5-48	5-70
150 μm	0-6	0-15	-	-	-

C=coarse: M=medium; F= fine

2.3.2 Chemical Properties

2.3.2.1 Chemical Composition

The determination of the total composition, organic and inorganic, of MSWI bottom ash, has two objectives; the first objective is to identity possible toxic elements and the other is to evaluate its potential uses. When the concentration of any toxic element exceeds the tolerable limits, MSWI-BA can not be re-used.

MSWI-BA contains a wide range of elements and compounds that make it difficult to determine the individual concentration of each element. Several analytical procedures and techniques have been developed to measure the individual concentration of elements and compounds (**29**). The analytical methods are based on the digestion of MSWI-BA samples by employing aggressive mixtures of chemicals, usually acids, which can break the bonds and thereby elements can be determined.

A wide range of metal concentrations in MSWI-BA has been reported. The inconsistency in metal compositions is attributed to sample heterogeneity, especially because a very small quantity of sample is used for the analytical procedure and the type of digestion chosen. In addition, differences in concentrations have been observed even for the same type of samples and digestion but employing different instrumental techniques.

Recognising the significant differences in elemental composition of MSWI-BA, it has been reported that over fifty elements can be identified. The concentrations of elements

found are comparable to concentrations of materials found either in the lithosphere or soils (**29**). In general, the elemental inorganic composition of MSWI-BA includes:

1. O, Si, Fe, Ca, Al, Na, K, C as major elements with concentration greater than 10,000mg/kg;
2. Mg, Ti, Cl, Mn, Ba, Zn, Cu, Pb, Cr as minor elements with a concentration range between 1000 and 10,000 mg/kg;
3. Sn, Sb, V, Mo, As, Se, Sr, Ni, Co, Cd, Ag, Hg, B, Br, F, I as trace elements with concentrations under 1000 mg/kg.

In addition, elements related to bio-geochemical cycles, such as C (organic), S, P, N are present in the MSWI-BA.

The major concern regarding the organic composition of MSWI-BA is due to the release of some trace organics classified as cancinogenics which include polychlorinated dibenzo-p-dioxines (PCDDs), polychlorinated dibenzo-p-furans (PCDFs) (**28**). The reported concentrations for these compounds are very low and below tolerable limits. High concentrations of these components have only been detected in individual incineration facilities where part of the MSWI-FA was mixed with MSWI-BA. Apart from the determination of organic trace elements, little work has been carried out to determine the total organic composition of MSWI-BA (**36**).

2.3.2.2 Loss on Ignition

Ignition reaction consists of burning a specific material at high temperature under an oxidising atmosphere. Consequently, any organic carbon and bound water are removed as carbon dioxide and water vapour respectively. Potential oxidation of a certain number of elements may also occur. Loss on ignition (LOI) is expressed as the percentage of mass reduction occurring after ignition at high temperature.

The LOI is a factor to be considered when assessing the performance of construction materials (**34,37,38**). For materials, such as fly ash, LOI includes the inorganic carbon content, $CaCO_3$, and combined water (**39**). High LOI in pozzolanic materials indicates poor pozzolanic activity. High LOI is associated with high content of inorganic carbon materials, which tends to form coarse particles, thereby, reducing the specific surface (m^2/kg) and the pozzolanic reactivity. For waste materials used as aggregates, high LOI is associated with high content of organic material and poor content of mineral material. Generally, high LOI values limit the use of waste as partial substitution of aggregates or cement.

LOI is a measure of the relative burnout material presented in the MSWI-BA. It has

been reported that up to 60% of the LOI in MSW-BA is organic carbon; the remainder is carbonates and tightly bound water of hydration (**40**). LOI values mainly depend on MSW input, combustion and operating conditions. These factors make it difficult to report an average value of LOI for MSWI bottom ash. Eighmy et al. (1992) (**32**) reported that there are two maximum LOI peaks in MSWI-BA. The first peak occurs with particles whose diameters are around 10mm due to the un-combusted char material and paper. The second peak occurs with particle less than 250 μm in diameter, indicating that this fraction contains a high proportion of organic materials.

2.3.2.3 pH

The measurement of pH is of great importance for many types of waste because pH values can determine the toxicity of materials. In addition, the pH is one of the most relevant parameters in controlling the solubility of compounds of MSWI-BA samples during hydration, carbonation and leaching reactions (**19**,**29**,**41**).

2.3.2.4 Acid Neutralisation Capacity

Acid neutralisation capacity (ANC) is defined as the capacity of a material to resist changes in pH (**28**). The ANC results are used to assess the mobility of specific compounds with variation in pH. Therefore, the buffer capacity is an important aspect in the leaching behaviour of MSWI-BA. The ANC of MSWI-BA is associated with calcium compounds (**41**). The high value of ANC for fresh MSWI-BA is attributed to release of soluble calcium salts (e.g. portlandite), whereas low value of ANC for ageing MSWI-BA is caused by less soluble calcium compounds, $CaCO_3$.

Although silicon, (Si) is one of the major components of MSWI-BA, there are indications that compounds containing Si do not considerably affect the ANC of MSWI-BA. It has been observed that Al and Fe do not affect the ANC of MSWI-BA as Si (**28**).

2.3.2.5 Dissolvable Solid Content

The dissolvable solid content is a measure of the soluble mineral content of MSWI-BA. Materials that are burnt completely exhibit high dissolvable solid content. Good combustion conditions leads to complete mineralisation of MSWI-BA thereby increasing the soluble mineral content. For modern incinerator facilities the dissolvable solid contents range from 3 to 14% (**42**).

2.3.3 Morphology and Mineralogy of MSWI-BA

Particle morphology and mineralogy are important factors in assessing the physical and chemical characteristics of MSWI-BA. The morphology of MSWI-BA is often

studied using Scanning Electron Microscopy (SEM). Typically, MSWI-BA is a light-weight porous aggregate with more angularity and more surface roughness and textures than many traditional aggregates (**28**). In addition, the high porosity of MSWI-BA provides a large surface for chemical reaction and leaching phenomena to occur.

Furthermore, properties (e.g. leaching, physical, mechanical and durability) of cement-based systems containing MSWI-BA are strongly dependent on the mineralogy of MSWI-BA. A high proportion of stable compounds such as silicates and oxides has a positive influence on engineering and leaching characteristics. The study of mineralogical composition is complicated due to the numerous mineral phases involved and the way they are bound. Table 2.4 provides the mineralogical composition of MSWI-BA reported in the literature (**43-46**) from different countries. In the table, mineral phases are given in order of decreasing abundance. Although chemical and mineralogical compositions of MSWI-BA vary largely it can be noticed that, generally the most dominant phases contained in the MSWI-BA are SiO_2, Fe_3O_4, $CaCO_3$, $CaSO_4 2H_2O$, $Ca(OH)_2$, $(Ca, Na)_2(Al, Mg)(Si, Al)_2O_7$, NaCl, KCl. No investigation was carried out wether these phases poses hydralic properties.

Table 2.4. Mineral phases in MSWI-BA (in decreasing order of abundance)

Stämpfli (43)	Vehlow et al (44)	Kirby et al. (45)	Eighmy et. al (46)
SiO_2	Fe_3O_4	SiO_2	$Ca_2Al_2SiO_7$
$CaCO_3$	SiO_2	$CaSO_4$ $2H_2O$	$MgCa_2Sl_2O_7$
Fe_3O_4	$(Ca, Na)_2(Al, Mg)(Si, Al)_2°_7$	$3(Al_2O_3)$ $2(SiO_2)$	Fe_3O_4
Fe_2O_3	$CaCO_3$	TiO_2	$FeAl_2O_4$
Fe^0	$KAlSi_3O_8$	Fe_2O_3	SiO_2
FeO	$NaAlSi_3O_8$	FeO	$Ca_3(PO_4)_2$
$Ca_2Al(OH)_7$ $6.5H_2$	$CaAl_2Si_2O_8$	$CaSO_4$	Fe_2O_3
$Na_2Si_2O_5$	$FeCr_2O_4$	KCl	$CaSO_4$
$CaSO_4$	$Ca(Mg,Fe)Si_2O_6$	NaCl	CaO
$(Ca, Na)_2(Al, Si)_2$ Si_8	Fe_2SiO_4		$Al(OH)_3$
$NaAlSi_3O_8$	Cr_2O_3		NaCl
	Fe_2O_3		$ZnCl_2$
	$CaMgSiO_4$		$NaAlSi_3O_8$
	Al_2O_3		Al_2SiO_5
	$Ca(OH)_2$		TiO_2

2.3.4 Influence of Ageing on MSWI-BA Properties

Since MSWI-BA is generated at high temperature and subsequently cooled, under atmospheric conditions, MSWI-BA is not stable and its mineralogical characteristics change with time.

During the natural ageing process of MSWI-BA, carbonation and hydration reactions take place. These reactions require time and continue even for several months or years. Chemically, MSWI-BA is very reactive due to free CaO which in the presence of moisture $Ca(OH)_2$ is formed. The following reactions start occurring during the quenching step of MSWI-BA prior to storage.

$$CaO + H_2O \rightarrow Ca(OH)_2 \leftrightarrow Ca^{+2} + 2OH^- \qquad \textbf{Reaction 2.1}$$

$$Ca(OH)_2 + SiO_2 \rightarrow CaO * nSiO_2 \qquad \textbf{Reaction 2.2}$$

The absorption of CO_2 by hydroxides causes a decrease in pH, and calcite precipitates until the equilibrium with atmospheric CO_2 is reached.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \textbf{Reaction 2.3}$$

Other reactions may occur during weathering of MSWI-BA such as:

$$Fe^0 + \frac{3}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe(OH)_2(insoluble) \qquad \textbf{Reaction 2.4}$$

In addition, others compounds such as $Al(OH)_3$ and amorphous aluminosilicates can also precipitate as a result of the decrease in pH during carbonation. Solubility of specific aluminium compounds can be affected when pH decreases from 10 to 8 (**47**). For example ettringite will pass to solution when pH drops below 10. Investigations of the effect of carbonation on trace element have shown that a significant leaching retention of some trace elements as carbonation reaction occurs (**48,49**). This lower leaching availability of MSWI-BA after carbonation may be due to the incorporation of trace elements into new formed phases (**48,49**).

The influence of ageing on MSWI-BA characteristics has been well documented (**24,31,43,44,47,50,51**). Although, there is no total agreement between all studies, in general it has been observed that a significant improvement related to civil engineering characteristics and reduction of soluble solids occur when the MSWI-BA is previously weathered. The increase in strength and improvement in durability properties are attributed to the formation of new mineralogical phases (e.g. gypsum and ettringite) that are more stable (**50,51**). The improvement in leaching behaviour of aged MSWI-BA stems from the formation of compounds that retain heavy metals. Zevenbergen et al.

(**52**) have identified the formation of a clay-like structure on which metals can be retained by ion-exchange effects.

Moreover, when MSWI-BA was used as road sub-base, cracking and blistering phenomena were observed as a result of hydrogen being generated. Hydrogen is formed according to following redox reactions, which occur with time (**53**).

$$2Al^0 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2(g) \qquad \textbf{Reaction 2.5}$$

$$Cu^0 + 2H_2O \rightarrow Cu(OH)_2 + H_2(g) \qquad \textbf{Reaction 2.6}$$

$$Zn^0 + 2H_2O \rightarrow Zn(OH)_2 + H_2(g) \qquad \textbf{Reaction 2.7}$$

2.3.5 Leaching Behaviour of MSWI-BA

A fluid used to extract compounds from solid samples is known as leachant or extractor fluid. A liquid resulting from the release of solid into leachants is known as leachates (**54**). The release of leachates depends on intrinsic characteristics of the solid phases (e.g. mineralogical and chemical compositions), leachants (e.g. pH,) and leaching procedure (e.g. liquid/solid ratio, leachant renewal times, temperature and duration of test and method of contact). Many leaching procedures have been developed to predict the leaching rate and mechanisms of waste placed in landfill sites or when they are used as substitute material. Classification and types of leaching test are discussed further in Chapter 5.

Knowledge of leaching behaviour of MSWI-BA in landfill or application sites is required to assess the potential risk to the environment. MSWI-BA can leach compounds when it is in contact with a fluid. The long-term leachability of heavy metals, sulfates and chlorides into the environment is the main concern with regard to utilisation or disposal of MSWI-BA.

The mobility of toxic elements and compounds contained in MSW-BA depends on its hydrological, mineralogical and geochemical characteristics. The hydrological aspects include physical properties of MSWI-BA such as homogeneity, permeability and porosity (**19**). Mineralogical properties are referred to each mineral in the materials. Geochemical properties include the interactions between the different constituents of MSWI-BA and the medium.

Mechanisms that control mobility of heavy metals, sulfates and chlorides are classified into two groups:

a) Mechanisms that enhance dissolution: The presence of ions that can break bonds of solid constituents is a common method to dissolve solids. Other reaction that encourages dissolution of heavy metal is the complexation reaction. Complexation reaction consists of moving certain metals from solid phase to the fluid solution in presence of specific ligans.

b) Mechanisms that limit solubility: Adsorption, ion-exchange and precipitation are included in this group of mechanisms.

The controlling parameters of the above mechanisms are the pH, the characteristics of major component of solid, known as the matrix, and type of bonds between metals, sulfate and chlorides and the matrix.

Adsorption phenomena are one of the most important mechanisms to limit or encourage dissolution of heavy metals and are equally influenced by the pH, the matrix and type of bonds. Hydroxides and oxides are ideal surfaces for adsorption of heavy metals, where metal ions coordinate with donor oxygen atoms from the surface. In this specific adsorption, cations are adsorbed in alkaline conditions and anions are neutral to acid conditions. Because MSWI-BA exhibits alkaline pH, anions are less immobilised than cations in ash deposits, as is illustrated in Figure 2.4 (**19**).

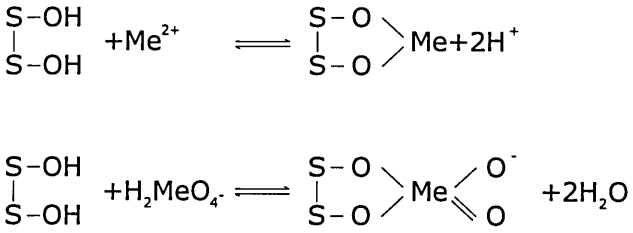


Figure 2.4. Adsorption of cation and anion metal compounds onto hydroxyl surfaces as a function of pH (19)

Precipitation/dissolution of heavy metal cations is strongly pH dependent whereas metal oxanions tends to be less dependent on pH. The precipitation of metallate salts controls the mobilisation of oxyanions. The metallate salts are not affected significantly by the pH (**19**). The following reactions show the pH dependence of oxyanions;

$$Me(OH)_2 + 2H^+ \Leftrightarrow Me^{2+} + 2H_2O$$ **Reaction 2.8**

$$CaMeO_4 + 2H^+ \Leftrightarrow Ca^{2+} + H_2MeO_4^{1-}$$ **Reaction 2.9**

Johnson (**19**) compared data of leachates from a landfill of MSWI-BA with theoretical equilibrium data. It was reported that the following solid phases were involved in the solubility of MSWI-BA constituents:

a) The concentration of Mo in leachates was controlled by the precipitation of calcium metallate salts, $CaMoO_4$.

b) Gypsum and ettringite may be the phases involved in the solubility of calcium and sulfate compounds in leachates.

c) The concentrations of Al^{3+} in leachates were attributed to the solubility of ettringite and gibbsite, $Al(OH)_3$.

d) The concentrations of silicon in leachates did not seem to be associated with equilibrium solubility of quartz or calcium silicate compounds.

e) The low concentration of Fe^{3+} in leachates was attributed the low solubility of iron compounds in the basic and neutral pH range that MSWI-BA deposits produce.

Moreover, Johnson et al. (**41**) studied the concentrations of Cu, Pb, Cd and Zn in leachates obtained from laboratory leaching procedures and from MSWI-BA landfill. For laboratory and field studies, MSWI-BA samples were not directly in contact with atmospheric CO_2, in order to reduce the carbonation process. The precipitation of metals as hydroxides and as carbonates was considered to be the dominant mechanism of solubility of metals despite the fact that metal cations may be associated with other anions (e.g. Cl^{1-}, SO_4^{2-} and organic ligans). The concentrations of metals obtaining from laboratory and landfill samples were compared with theoretical equilibrium concentrations of metals as hydroxides and carbonates. Metal concentrations were plotted against pH values. Theoretical concentration/pH curves were calculated considering the thermodynamic stability constants and the release of competitive ions (Cl^{1-}, SO_4^{2-}, Ca^{2+}). The following results were reported:

a) The lowest concentrations of each metal cation were observed in the neutral to basic pH range (from 7 to 14). The maximum concentrations of each cation in leachates were lower than the total metal content in the original MSWI-BA samples. This indicated that the remaining metal contents are bound within insoluble matrices.

b) The solubility of Cd in landfill and laboratory leachates appears to be controlled by the precipitation of $CdCO_3$. The higher solubility of Cd in field samples is attributed to the formation of chloride complexes.

c) The concentrations of Cu in laboratory and field leachates cannot be explained as results of precipitation either of $Cu(OH)_2$ or of $CuCO_3$.

d) The concentrations of Zn and Pb in leachates indicated that interactions with solid phases may control their solubility, because their concentrations cannot be explained as results of precipitation of either their hydroxides or carbonates.

During the ageing process of MSWI-BA, pH and adsorptive properties of the matrix change (see section 2.3.4) (**19**), thereby, leaching behaviour of MSWI-BA will be affected for these changes of pH. Meima et. al. (**49**) assessed the effects of the ageing process of MSWI-BA samples on leaching behaviour of Cd, Pb, Zn, Cu and Mo. They observed, for all the elements examined, a reduction in leaching with time due to the decrease in pH and the formation of less soluble compounds. For fresh MSWI-BA samples, precipitation/dissolution seems to be the dominant mechanism, whereas for mature samples the adsorption of Cd, Pb, Zn, Cu and Mo onto the surface of new minerals formed appears to be the likely controlling mechanism. However, precipitation reactions cannot be totally excluded in matured samples. Controversially, Bodénam et al (**55**) observed an increase in sulfate solubility of mature MSWI-BA samples due to the decrease of pH as the ageing process continued.

2.3.6 Current Utilisation of MSWI-BA

It has been estimated that the amount of MSWI-BA generated is increasing throughout the world. In the UK around one million tonnes is generated annually. This large quantity of MSWI-BA produced encourages its possible utilisation in construction as aggregate.

MSWI-BA may possess higher concentration of soluble pollutants and generally exhibits higher freezing-thawing susceptibility than other waste used as construction material (**56**). However, these facts do not restrict completely the utilisation of MSWI-BA as an alternative material.

MSWI-BA can be used as unbound and bound materials. Unbound MSWI-BA is used in roads predominately for sub-grade, capping layer and sub-bases (**57**). Recently the use of unbound MSWI-BA is being restricted and discussed widely due to its impact on human health and the environment as a result of the leaching of pollutants including heavy metals (e.g. Cd, Zn, Cu, Cr, and Hg) and anions (e.g. chlorides and sulfates).

Bound MSWI-BA applications include concrete/brick blocks, cementitious and bitumen sub-bases in roads (**58**). Cement-based systems and bitumen can significantly reduce the human health and environmental risk by immobilising the heavy metals. Cement reacts with ash and chemically bonds metal ions into the mixture whilst bitumen encapsulates metals (**57**,**58**). Work on MSWI-BA bound with cement matrix, as a replacement of aggregate, have indicated the need for increasing binder contents to achieve similar strengths and frost resistance (**57**,**59**) to natural aggregates. However, an appropriate selection of cement may reduce the binder content. Investigations on bound MSWI-BA mixed with bitumen are not consistent; some authors (**57**) have

reported that bitumen mixtures incorporating MSWI-BA do not need increased amounts of binder. Others have observed that MSWI-BA used as aggregates and mixed with asphalt concrete, requires additional asphalt. The need for additional bitumen is due to the higher porosity of MSWI-BA compared to conventional aggregates (**60,61**).

For either unbound or bound applications, it is recommended to process and treat the MSWI-BA prior to utilisation in order to improve its engineering properties and environmental acceptance. The processing currently employed involves the separation of ferrous and non-ferrous materials (with possible re-use), screening, removal of unburned organic matter and the natural ageing process. Washing stages coupled with injection of CO_2 have been investigated to accelerate the ageing process of MSWI-BA. The removal of soluble salt and fine particles has resulted in a significant improvement in the civil engineering properties (**56**). The use of large amounts of CO_2, also reduced significantly the leachability of metals (**56**).

For applications or disposal of unwashed MSWI-BA, it is recommended to be stored at ambient conditions for at least three months in order to improve its stability (**57**).

2.4 CHEMISTRY OF CEMENT-BASED SYSTEM

2.4.1 Chemistry of Cement

Lime, silica, alumina and iron oxide are the main constituents of Portland cement. These compounds interact with each other forming calcium silicates, $2CaOSiO_2$ and $3CaOSiO_2$ (C_2S and C_3S), tricalcium aluminate, $3CaOAl_2O_3$ (C_3A), and tetracalcium aluminoferrite, $4CaOAl_2O_3Fe_2O_3$ (C_4AF). In addition, there are other minor compounds, such as MgO, TiO_2, Mn_2O_3, K_2O, Na_2O, small residue of un-combined lime, known as free lime, and gypsum ($CaSO_42H_2O$). The K_2O and Na_2O, known as alkalis, are of particular interest because of their possible influence on strength development and reaction with aggregates. A specific amount of gypsum is added during the manufacture of cement to extent the period of plasticity that is required during earlier stages of hydration. Gypsum reacts with C_3A thereby retarding its hydration.

Table 2.5 gives an average for the oxide and phases compositions of Ordinary Portland Cement (OPC) (**39**). Small changes in the concentration of raw oxides cause considerable variation in the C_3S/C_2S ratio and in the contents of C_3A and C_4AF (**62**). In addition, when the sum of the two silicates (C_3S and C_2S) varies slightly, the variation in the C_3S/C_2S ratio depends on the CaO/SiO_2 (C/S) ratio of the raw materials (**39**).

Table 2.5 Common Composition of OPC

Contents (% by weight)t			
CaO	60-67	**C_3S**	54-55
SiO_2	17-25	**C_2S**	16-17
Al_2O_3	3-8	**C_3A**	10-11
Fe_2O_3	0.5-0.6	**C_4AF**	9-10
MgO	0.5-4		
Alkalis	0.3-1.2		
SO_3	2-3.5		
Insoluble residues	1.5-5[a]		
Loss on ignition	3-5[a]		

a BS ENV 197-1:1992(**63**)

The reaction of cement with water, known as cement hydration, is quite complex and not fully understood (**64**). The hydration of cement is controlled by surface, near-surface and interfacial phenomena. Two models have been proposed to explain the formation of hydrated cement; i) the gel or osmotic model and ii) the crystalline model, both of which are reported in depth elsewhere (**64**).

The hydrated products include crystalline phases (e.g. portlandite and ettringite) and amorphous phases. The latter consists of gel phase of calcium silicate hydrate, $3CaO2SiO_23H_2O$ (C-S-H). Calcium silicate hydrates are the principal constituents of hydrated cement, approximately 60% to 70 % (**64**). The hydration of cement also leads to the formation of 20% to 25% calcium hydroxide and 5% to 15% of other solid phases (e.g. calcium aluminate and ferrite hydrates) (**64**). Strength and durability properties of cement-based systems are significantly associated with the calcium silicate hydrates (**39**,**65**). Also, other compounds such as C3A and gypsum affect these properties.

The hydration reactions of C_3S and C_2S are shown below:

$$2(3CaOSiO_2) + 6H_2O \rightarrow 3CaO2SiO_23H_2O + 3Ca(OH)_2$$ **Reaction 2.10**

$$2(2CaOSiO_2) + 4H_2O \rightarrow 3CaO2SiO_23H_2O + Ca(OH)_2$$ **Reaction 2.11**

Some physical observations have indicated that C_3S and C_2S hydrates may form different types of calcium silicate hydrate (C-S-H) (**39**). However, clear evidence on the distinctive structure of C-S-H formed from C_3S and C_2S has not been reported yet.

Therefore, it is considered that both components (C_3S and C_2S) form the same type of C-S-H (**39**). Calcium silicate hydrates are able to accommodate small amounts of Al, Fe, Mg and other ions and varying amounts of lime without causing significant changes in the structure.

The presence of a certain amount of C_3A is required during the manufacture of cement to reduce the burning temperature of clinker and to facilitate the combination of lime and silica. In addition, it has been observed that C_3A has the capacity to bind chlorides thereby reducing the amount of chlorides in the pore fluid (**39**). However, there are detrimental effects associated with the presence of C_3A in cement. The high rate of the hydration reaction of C_3A leads to rapid stiffening of the paste and thereby reducing the formation of C-S-H hydrates. Calcium aluminate hydrates (C-A-H) do not have a significant influence on the properties of hydrated paste, apart from the contribution of strength at early age (**39**). Reaction 2.12 shows one of the most probable forms of calcium aluminate hydrate (C-A-H) existing in the hydrated cement.

$$3CaOAl_2O_3 + 6H_2O \rightarrow 4CaOAl_2O_313H_2O \qquad \textbf{Reaction 2.12}$$

The hydration of C_3A is retarded and reduced by adding small amounts of gypsum. Gypsum reacts with C_3A to form insoluble calcium sulfoaluminate, ettringite (AFt) ($3CaO.Al_2O_3.\ 3CaSO_4.32H_2O$), on the surface of the C_3A grains. Thus, the formation of ettringite avoids the direct hydration of C_3A (**66**).

$$3CaOAl_2O_3 + 3CaSO_4 2H_2O + 30H_2O \rightarrow 3CaOAl_2O_33CaSO_432H_2O \qquad \textbf{Reaction 2.13}$$

Reaction 2.13 normally occurs in the early stages of hydration and it is completed when gypsum or other calcium sulfate compounds are depleted. Although, the formation of AFt is expansive, it does not cause important structural problems when this occurs during the plastic state of the cement hydration reaction. The formation of ettringite contributes to the early strength. However, if the same reaction occurs during the hardened state, ettringite will not be accommodated easily in the hydrates. This can cause cracking of the cement matrix and subsequently a loss in strength. The later formation of ettringite can occur when the remaining C_3A, which is due to an excess of C_3A content in the cement, reacts with external sulfates from the medium.

The level of gypsum is an important parameter to control the detrimental effect associated with either delay or excessive formation of ettringite. Gypsum content depends on three parameters; C_3A content, content of alkalis and fineness of cement particles (**67**). High contents of C_3A and alkalis coupled with fine particle distribution

require a high content of gypsum. Different equations have been developed to calculate the optimum gypsum content considering the above three parameters (**68**,**69**). It has been observed that increasing the gypsum content increases the amount of C-S-H formed but decreases its intrinsic strength. This loss in strength was associated with high C/S ratios observed in the hydrates (C-S-H) formed in the presence of a high concentration of gypsum. High C/S ratios lead to low surface area of C-S-H. The decrease of surface area may be linked with the tendency for calcium compounds to form large particles (**70**). The C/S ratio in C-S-H ranges between 1.8-2.0 in well made hydrated cement paste while in composite cement it can decrease down to 0.9 (**39**).

Calcium aluminate ferrite (C_4AF) does not have a significant effect on the properties of hydrated cement compounds. It has been reported that C_4AF compounds hydrate into C-A-H and calcium ferrite hydrate (C-F-H) compounds and they can react with sulfate ions to give similar reactions to C_3A (**39**,**66**).

2.4.2 Pore Water Composition

The excess water, which is not required for hydration reaction, is located in the un-filled space created by hydrated compounds and is known as pore water. Alkalis are the major components in the pore water. It has been reported that 40 to 60% of Na^+ and 50 to 70% of K^+ are present in the pore water for Portland cement paste (**65**). The positive charge of alkali ions in the pore fluid is mainly balanced by hydroxyl ions, OH, because other anions (e.g. sulfate, silicate, and aluminate), which are also present in cement-based systems, are insoluble or nearly so. The presence of hydroxyl ions raises the pH between 13 and 14 in the pore water. As consequence of the high content of hydroxyl ions precipitation of $Ca(OH)_2$ may occur. The precipitation of Portlandite and/or other lime-rich compounds causes a reduction of Ca^{2+} in the pore water thereby limiting further reactions that may require Ca^+ (**65**,**71**).

The content of alkalis in pore water is affected by the chemical composition of binders, type of aggregates and water/cement (w/c) ratio (**65**). In general, binders containing high content of alkalis present high alkali content in the pore water. However, binders containing pozzolanas (e.g. fly ash, slag) may present higher alkali content in their chemical composition than binders made exclusively with cement, but the alkali contents in the pore fluid may be lower than that for cement binders (**72**, **73**). The reduction in the alkali concentrations in pore water is due to the adsorption of alkalis on hydration products. The consumption of $Ca(OH)_2$ by the silica of pozzolanic materials, encourages the adsorption of alkalis when there is a lack of calcium (section 2.4.3).

The concentration of alkalis increases when the volume of pore water becomes smaller. The volume of pore water depends on w/c ratio and aggregate content; low w/c ratio and high aggregate contents decrease the volume of pore water and consequently increase the concentration of alkalis (**65**). On the other hand, the concentration of alkalis in pore water decreases in the presence of reactive silicate compounds contained in the aggregates. This phenomenon is called alkali-silica reaction (see section 2.4.4).

Taylor (**74**) summarised data on pore fluid of cement pastes and reported the following findings about the distribution or partition of alkalis between solid phases and pore water:

1. Alkalis were mainly bound into C-S-H. Since there was no evidence on which hydrated compound was involved on alkali adsorption and as C-S-H is the major constituent of cement hydrates, it can be assumed that alkalis are bound to surface of C-S-H hydrates.
2. Sodium, Na, was better bound into solid phases than potassium, K. Thus, the higher influence of Na compared with K on strength at earlier ages might be caused by the better adsorption of Na into hydrates and thereby less amount in the pore water (**39**).
3. The variation of alkali contents in clinker within a certain range did not significantly affect the distribution of alkalis between solid and pore water.

Sung and Glasser (**75**) observed similar partition of alkalis between the pore water and solid phases for different C-S-H phases prepared with concentrations of NaOH and KOH ranging from 1 to 300mM. However, the partition of alkalis was significantly dependent on the C/S ratio of the C-S-H. The lower the C/S ratio, the lower the alkali concentration in aqueous phase. The better alkali binding capacity at low C/S ratio is explained assuming that alkalis are bound to relatively acidic silicol sites (Si-OH). Acidic silicol sites are neutralised by reaction with either K or Na. The concentration and acidity of silicol groups increase as the C/S ratio decreases. In order to balance the increase of negative charge, alkalis are adsorbed, thereby, reducing their concentrations in pore water. Although Taylor (**74**) indicated that Na is better adsorbed than K, Sung and Glasser (**75**) found a similar binding capacity of sodium and potassium as was expected according to the similarity of their electro- negativities. This discrepancy between both experimentations was justified by the use of synthetic C-S-H in Sung and Glasser studies (**75**) and real cementitious materials in Taylor's work (**74**).

In addition, Sung and Glasser (**75**) reported that the presence of aluminosilicate in binders reduces significantly the concentration of alkalis in pore water by the adsorption of alkalis into C-A-S-H hydrates. That fact is explained assuming that Si can be substituted by Al^{3+} ions and other ion of Na^{+} or K^{+}. Reduction in alkali concentration in pore water can also be expected in the presence of ferro-silicates.

The significant influence of alkali content on gypsum requirement has been investigated by a number of authors (**39,65,71,76**). Jawed et al. (**71**) compiled and summarised the existing literature based on the effects of alkalis on the chemistry of cement and cement hydration reaction. They reported the following findings:

1. High level of alkalis in cement reduces the retardation of C_3A hydration (by ettringite formation).
2. Gypsum reacts more rapidly with cement containing high concentration of alkalis.
3. Cements with high concentration of sodium require more gypsum than cements with high potassium content.

The loss of retardation of C_3A hydration is probably due to the high pH levels generated by the alkalis, which tend to either destabilised ettringite or influence its mode of formation. It has been observed that alkalis are present in the aluminate phases. Aluminate phases containing alkalis hydrate and react with gypsum more quickly than aluminate phases without alkalis or low alkali content. The difference in gypsum requirements for sodium and potassium contents may be assumed by the fact that sodium exhibits higher affinity for aluminate phases than potassium does (**71**).

The influence of alkali contents on engineering properties of cement-based systems is not yet clearly understood (**39**). High concentration of alkalis in pore water is associated with low strength of cement-based systems (**76**). Some works (**39,71**) have reported that the presence of alkali increases the early strength and decrease the long-term strength. The decrease in long-term strength might be due to possible alkali-silicate reaction of alkalis and aggregates and to the heterogeneity of the microstructure of C-S-H caused by the incorporation of alkalis (**65,71**). However, others (**76**) have reported an overall increase in strength in the presence of alkalis. Alkalis seem to act as catalysts in forming C-S-H from silica and lime by forming sodium silicates which react with $Ca(OH)_2$ to form C-S-H.

2.4.3 Influence of Blending Materials on Cement Hydration Reaction

The use of some waste materials as a partial replacement of cement is becoming common practice in the construction industry. The most popular wastes used are mainly ground granulated blastfurnace slag (GGBS) from iron industry and fly ash from coal power station and silica fume, (pfa). Recently other wastes such as desulphurisation products and MSWI ashes are being investigated to be used to reduce the use of natural resource and avoid landfill tax (**77**).

In general, the wastes mentioned above have higher contents of SiO_2, Al_2O_3, iron oxides and sulphur content than cement (**65**). The common characteristic of all these materials is that they have a reactive siliceous or siliceous aluminate glassy phase. The reactive siliceous phase reacts with the products of cement hydration (e.g. $Ca(OH)_2$) in the presence of moisture, to form hydrated compounds that possess cementitious properties (**78**). This reaction is known as pozzolanic reaction and the materials that give this reaction are known as pozzolana. During the initial stage of the pozzolanic reaction, the Si-O-Si bonds of the glassy phases of pozzolana are hydrolysed by hydroxyl ions, OH^-, of the activators (e.g. $Ca(OH)_2$). Once the glassy network is disrupted, reaction between hydrolysed siliceous material and activator components occur forming hydrates that, in part, replace the anhydrous grains and, in part, fill the space between grains thereby developing a bond. At its simplest the reaction may be presented as follows (**77**);

$$Ca(OH)_2 + SiO_2(pozzolana) \rightarrow C-S-H \qquad \textbf{Reaction 2.14}$$

The pozzolanic reaction is mainly affected by the chemical composition (mainly reactive SiO_2, glassy,) and fineness (e.g. specific surface area (m^2/kg)) of pozzolanic material. Pozzolans are natural or waste materials containing high content of amorphous siliceous or silico-aluminous compounds or a combination thereof (e.g silica-fume and fly ash). Fly ash reacts differently than slag as a result of the combination of hydraulic and pozzolanic properties of slag. Slag generally contains CaO, MgO and reactive silica. Blended materials containing fly ash with high surface area can exhibit similar strength to blends made with slag at the same replacement levels (**77**).

The use of pozzolanic materials in binders affects the mineralogical composition, mechanical, physical and durability properties of hydrated compounds. The impact of blending materials on the properties is a function of the level of replacement. Cement is frequently replaced by slag up to 70%, and therefore, the characteristics of slag material will control the properties of the composite binder.

Replacement materials are more silica-rich than cement and the resulting hydrates are chemically different. One of the chemical modifications includes the reduction in C/S ratio of C-S-H gel. The reduction in C/S ratio encourages the adsorption of alkalis especially Na. Even if all alkalis were adsorbed, the pH would not decline below 12.4 due to the buffer capacity of the pair $Ca(OH)_2$-C-S-H. As replacement materials react with $Ca(OH)_2$, there is reduction or even elimination of portlandite as buffer agent and consequently the pH decreases in the pore water (**79**). The decrease in pH of the pore water is one of the main effects observed when blending materials are used in binders. One advantage of the slightly low pH is the reduction of alkali-silica reaction that can occur. Nevertheless, the pH reduction in pore water does not always occur. Diamond et at (**80**) observed that for composite binder containing ashes that possessed high level of CaO and low concentration of alkalis, the pH of pore water was higher than for plain cement. The high pH values of composite binder indicated high concentration of alkalis despite that ash contained low concentrations of alkalis. For this composite binder, the content of CaO from the ash buffered possible changes in pH in pore water.

It has been proven that the major benefit of using blending materials is physical improvements; more efficient packing of space within particles coupled with small size of pore size can reduce the permeability of cement-bases systems (**77**). In addition, there is evidence that some blended cement-based systems immobilise toxic compounds better than plain cement systems (**77**,**81-82**). Controversially, Li et al. (**83**) observed an increase in mobilisation of Cu, Zn and Pb when cement was partially replacement by fly ash. This fact was explained as a result of adding fly ash that caused the decrease in pH of pore water. These metals generally increase their solubility as pH decreases. This effect is discussed in detail in section 2.4.5.

The use of composite replacement materials has some disadvantages such as slow strength gain and a great sensitivity to curing condition. In addition, waste materials may present high concentrations of aluminate compounds and CaO, which may react with sulfates to form ettringite at later stages. This is discussed in section 2.5.4. Other undesirable constituents that can be present are free lime (CaO) and MgO, which cause delayed expansion as ettringite (**77**). Free CaO intercrystallised with other compounds does not react completely with water before setting and it can react later causing an increase in volume and subsequent expansion which can produce cracking. Magnesia reacts with water in a manner similar to CaO. There are two forms of MgO (crystalline and glass) and only the crystalline phase can be deleterious (**39**).

2.4.4 Alkali Silica Reaction

A reaction of certain aggregates with hydrated cement paste is known as alkali-silica reaction (ASR). It consists of reaction between reactive forms of silica (e.g. opal, chalcedony and trymite) from aggregates and alkali hydroxides in pore water (**33**). The reaction starts when hydroxide ions attack the silica and SiO^- groups are formed. The SiO^- groups balance their negative charge with the most available cations, K^+ and Na^+, forming an alkali silicate gel. The alkali silicate gel can imbibe water causing an increase in volume (**84**). Since the gel is formed in a confined space, therefore an internal pressure is created that causes cracking and disruption of the hydrated structure.

The ASR depends on the reactivity of aggregates (type of silica), the moisture content, the alkalis content in the pore water and permeability of hydrates (**33**). The reactivity of aggregates is affected by particle size and porosity. The effects of ASR may be observed within days or after years of hydration.

The utilisation of waste with pozzolanic properties as partial replacement of cement is one of the well-established methods to minimise the expansion due to alkali-silica reaction (**85-88**). The greater improvement in reducing the impact of ASR compared with binders containing plain cement is due to the adsorption of alkalis. The adsorption of alkalis is caused by the reduction in calcium that is consumed in the pozzolanic reaction (see section 2.4.2).

Moreover, it has been observed that ash containing high concentrations of alkalis exhibited higher alkali concentrations in pore water than plain cement. However, this ash produced less expansion due to alkali-silica reaction than plain cement. The reduction in ASR effects is attributed to the reduction in the available calcium in the system (**86,87**). This supports the hypothesis that the alkali-silicate gel can only be formed in the presence of Ca^{2+} ions (**33,84**).

2.4.5 Behaviour of Metals in Cement-Based Systems

There are two factors that have encouraged investigating the behaviour of metals in cement-based systems. Firstly, there is a need to determine the efficiency of solidification/stabilisation methods that are based on binding waste with cement. Secondly, there is a need to understand the influence of metals on the hydration and long-term leaching performance of cement-based systems. Nevertheless, many fundamental aspects remain poorly understood due to the different parameters involved (**79**).

Metals can be physically and/or chemically bound to the cement matrix. Chemical and physical mechanisms can occur either simultaneously or sequentially and a clear distinction between physical and chemical mechanisms is not always possible. These mechanisms as well as the hydration of cement are strongly controlled by surface, near surface and interfacial phenomena (**64**).

The possible interactions between metals and the cement matrix have been discussed in depth by different researchers (**89- 92**). The immobilisation of metals in cement-based systems is attributed to the alkaline nature of this system and buffering capacity provided by $Ca(OH)_2$, and C-S-H hydrates. Considering the high alkaline pH of the cement-based systems, most of the metals might exist as metal hydrated phases (Me H_2O), metal hydroxides ($Me_n(OH_m)$) and/or calcium metal salts.

The fundamental physical-chemical processes involved in the immobilisation of metals in cement-based systems are as follows (**83,93**).

1. Precipitation of metals.
2. Adsorption of metals onto the surface of C-S-H compounds or other hydrated phases (e.g. C-S-A-H).
3. Encapsulation of metals into C-S-H phases.
4. Incorporation of metals into crystalline phases of ettringite.

The analysis of a number of experimental studies demonstrates differences on how metals contained in waste interact with cement-based systems. Thus, Glasser (**79**) reported that most cationic elements with a charge of +3 or more are more strongly bound to the cement matrix than anionic compounds. At low concentrations, the solubility of cationic and anionic species is controlled by adsorption onto C-S-H sites. At high C/S ratios, C-S-H has a positive surface charge and adsorbs mainly anionic species. However, due to high abundance of anions in cement (OH^-, SO_4^{2-}, etc) there is competition for sorption sites between anionic constituents of cement and anionic species of waste and therefore toxic anionic species are generally poorly adsorbed. At low C/S ratios C-S-H tends to adsorb cations which do not need to compete actively for sorption sites. Irrespective of C/S ratio, C-S-H compounds have a range of sorption sites so that cations are never adsorbed to the exclusion of anions and vice versa. For example, arsenites occurring as AsO_4^{2-} or AsO_3^{2-} are less bound compared with other toxic cationic compounds. Despite that arsenates, AsO_4^{2-}, may substitute SO_4^{2-} in hydration products, the partition coefficients between aqueous and solid phases do not indicate good binding capacity.

Moreover, metal species with structure type MeO_4^{2-} present better immobilisation performance than structure type MeO_3^{2-}. Vandecasteele et al. (**94**) examined the leaching behaviour of fly ash containing high concentration of As(III). Fly ash containing As(III) was stabilised with cement and lime. Stabilised fly ash was subjected to a leaching procedure to examine its leachability after stabilisation. They found that concentration of As(III) in leachates was lower when fly ash was oxidised with H_2O_2 before stabilisation. The oxidation consisted of the conversion of As(III) to As(V). Both, As(III) and As(V), react with lime and cement forming $CaHAsO_3$ and $Ca_3(AsO_4)_2$ respectively. Vandecasteele et al. reported that the higher concentration of As in leachates of systems containing non-oxidised fly ash compared with oxidised fly ash systems was due to the higher solubility of $CaHAsO_3$ compared with $Ca_3(AsO_4)_2$.

Glasser (**79**) also discussed the mechanisms involved in the immobilisation of Cr(III) in cement-based systems. Considering the precipitation of $Cr(OH)_3$, the mechanism that controls the partition of Cr(III) between the solid and aqueous phases, it was observed that the concentration of Cr(III) in pore fluid was several magnitudes smaller than expected. This discrepancy is attributed to the partial replacement of Al(III) atoms in calcium aluminate hydrate by Cr(III). Thus, the solubility of Cr(III) is controlled by the solubility of calcium chromium-aluminium hydrates. The partial replacement of Al(III) by Cr(III) may not be as rapid, and initially, Cr(III) may precipitate as $Cr(OH)_3$ while calcium chromium-aluminium hydrates may require either weeks or months to form. During these weeks or months the solubility of Cr(III) in pore water will be continuously decreasing.

Roy and Cartledge (**95**) suggested that copper exists mainly as hydrated hydroxides and/or complex calcium compounds in cement-based systems. The solubility of Cu may be controlled by precipitation and adsorption mechanisms.

Park and Batchelor (**96**) investigated the pore water concentrations of Cd(II), Cr(VI), Pb(II) and Hg(II) in 28 day old Portland cement paste. Different ranges of doped metal concentrations and w/c ratios were examined. Heavy metals were added into water in the form of $Cd(NO_3)_2$, Na_2CrO_4, $Pb(NO_3)_2$, and $Hg(NO_3)_2$. Concentrations of heavy metals in the pore fluid were compared with those concentrations obtained using a theoretical model. This model is known as SOLTEQ (**97**) and is used to predict the most likely solid phases, dominant aqueous species and equilibrium concentrations for each heavy metal. SOLTEQ model assumes that precipitation is the controlling mechanism of immobilisation of heavy metals. Results showed that only the concentration of Hg(II) in pore water was similar to that expected considering the precipitation of the most likely solid phase (HgO) as the controlling or dominant

mechanism. The concentrations of Cd(II), Cr(VI) and Pb(II) in the pore water were smaller than those expected considering precipitation as the controlling mechanism. Therefore, other mechanisms such as adsorption of their anionic forms (CrO_4^{2-}, $Pb(OH)_4^{2-}$, and $Cd(OH)_4^{2-}$) onto some solid phases or lattice substitution (e.g. CrO_4^{2-} in place of SO_4^{2-} in ettringite, replacing Ca containing crystalline phases by Pb) must dominate the immobilisation of these heavy metals. In addition, Wang et. al (**98**) also suggested that the immobilisation of Cr(VI) for cement-based systems was achieved due to the formation of a complex calcium chromate compound with low solubility.

Park and Batchelor (**96**) also examined the adsorption behaviour of alkalis in pore waters. The concentration of K in pore waters indicated that adsorption is not the mechanism that controls immobilisation. They suggested that the precipitation/dissolution of some potassium compounds, which were strongly dependent on pH, may control potassium concentrations in pore waters. Concentration of sodium ions in pore water can be explained as a result of adsorption onto the surface of C-S-H. Figure 2.5 depicts the hypothesis for adsorption of metal anions facilitated by strong Na adsorption on the surface of C-S-H. Na ions adsorb onto the negative charged silica surface of C-S-H and build a strong layer with positive charge. The positive layer facilitates the adsorption of metal anions (e.g. CrO_4^{2-}, $Pb(OH)_4^{2-}$, and $Cd(OH)_4^{2-}$) mainly by electrostatic interaction. In addition, it was found that the amount of each of these metals removed from pore waters increases dramatically with increase in the adsorbed sodium. This indicates that the adsorption of metals anions is directly related to that of Na.

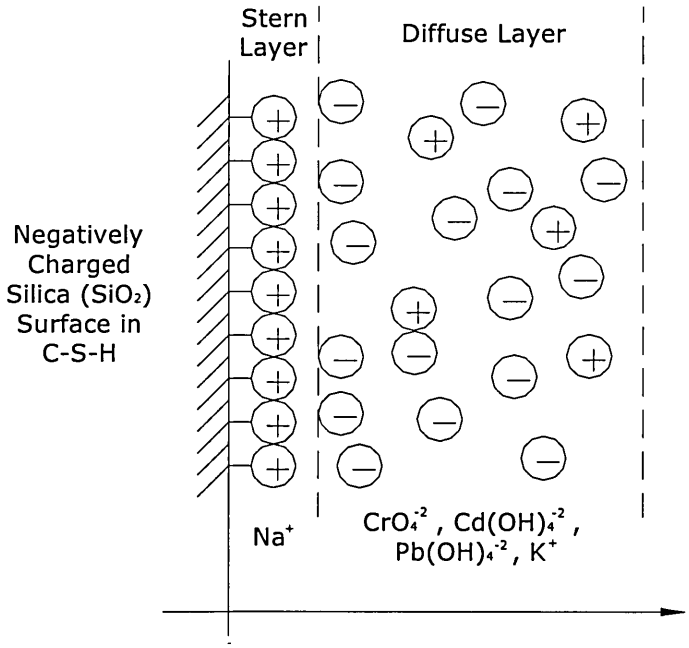


Figure 2.5. Adsorption of Na onto negatively charged C-H-S surface and adsorption of metal ions onto Na Layer in pore water of plain cement

Zinc is expected to form hydroxides in cement-based systems due to the high pH condition. As a result of the amphoteric function of Zn hydroxides, as shown by Reaction 2.15, they may be adsorbed onto the negative surface of C-S-H hydrates and/or form calcium zinc complex hydrated compounds such as ($CaZn_2(OH)_6H_2O$) (**83**).

$$Zn^{+2} + 2OH^{-1} \rightarrow Zn(OH)_2 \rightarrow 2H^{+2} + ZnO_2^{-2} \qquad \textbf{Reaction 2.15}$$

Recent studies have demonstrated that retardation and in some cases restriction of cement hydration result from the addition of waste containing metals (e.g. Zn, Cd, Pb, and Cr) (**64,82,98-100**). The retardation of hydration and setting is due to coating of the surface by calcium metal hydrates formed immediately after contact with water. As a consequence of the high pH of cement hydration reaction, the newly formed C-S-H phases possess a negative charge that is compensated by Ca^{2+} ions. In the presence of metals a negative layer of metal hydroxyl anions (e.g. $Zn(OH)_4^{2-}$, $Zn(OH)_3^{1-}$, $Cd(OH)_4^{2-}$, $Pb(OH)_3^{1-}$ and $CrO4^{2-}$) is formed, next to the positive layer of calcium ions. Metal hydroxyl anions are transformed into calcium metal hydrates (e.g. $CaZn_2(OH)_6H_2O$, $CaCd_2(OH)_4$) that cover the cement grains and retard the cement hydration.

Asavapisit et al. (**100**) discussed the influence of Pb, Zn and Cd contained in a synthetic waste, on the hydration reaction of cement. They observed that the Pb from the waste reduced the concentration of Ca^{2+} and SO_4^{2-} in pore water compared to plain cement. This reduction in concentrations of Ca^{2+} and SO_4^{2-} indicated that either the dissolution of gypsum was inhibited or ettringite was rapidly formed. Since SO_4^{2-} ions remained in solution after 24 hours of hydration, the reduction in Ca^{2+} and SO_4^{2-} concentrations was due to limitation of formation of calcium sulphoaluminates (e.g. ettringite) (**100**). Because the hydrated C_3A surfaces were also rapidly coated with $Pb(OH)_3^{1-}$, like C-S-H phases the formation of calcium sulphoaluminates was limited. The behaviour of zinc was similar to Pb, except Zn was rapidly hydrolysed and adsorbed onto solid phases causing a severe retardation of hydration due to the formation of an impermeable membrane coating the cement grains. It was observed that the formation of $Ca(OH)_2$ was limited during the first 28 days and that SO_4^{2-} ions were removed from solution more rapidly than during hydration of plain cement. This indicated that $CaZn_2(OH)_6H_2O$ phases do not only coat cement particles but also gypsum particles limiting the gypsum dissolution. The major effect observed for the addition of Cd was the increase in the initial rate of $Ca(OH)_2$ formed despite the formation of $CaCd_2(OH)_4$ on the surface of the hydrates. However, for samples cured for longer than 24 hours, the concentrations of $Ca(OH)_2$ in the samples were similar to

those found in control samples. Thus, the effect of Cd in the cement hydration was different than that of Zn.

Figure 2.6 shows the mechanisms that may be involved in solidification/stabilisation of heavy metals methods using cement-based systems (**101**). The figure shows a cement grain surrounded by the newly hydrated products, C-S-H and indicated the most likely mechanisms that control the interaction between the cement-based system and various metals. For example, the likely mechanisms suggested are that Cr is incorporated into C-S-H structures, other metals such as Cd and Zn form calcium compounds on the surface of C-S-H, and Pb and Hg precipitate on the surface of C-S-H.

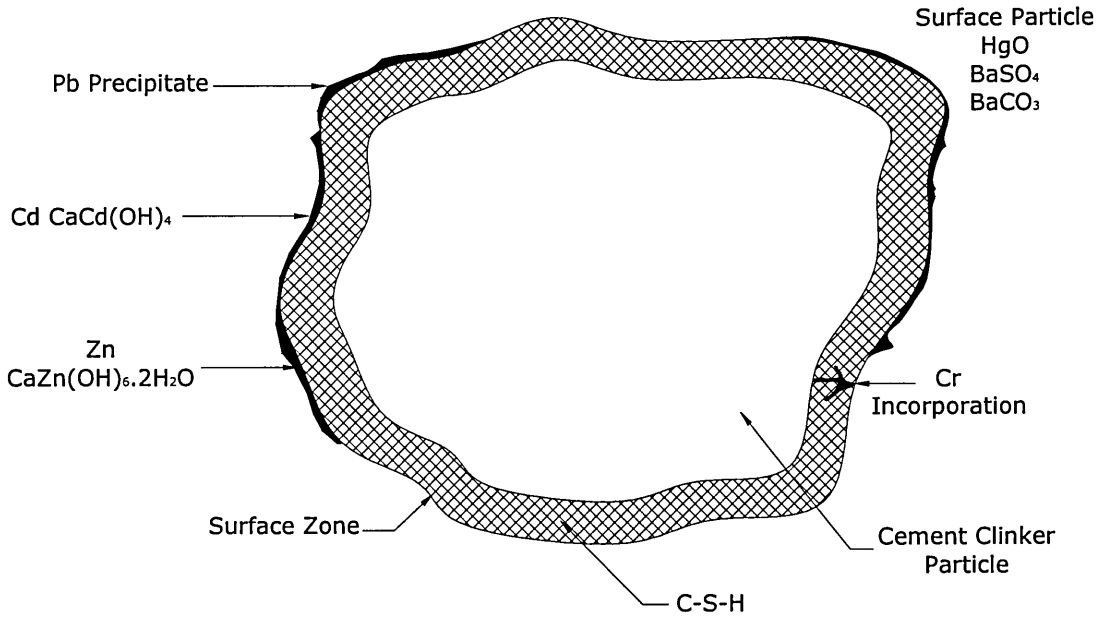


Figure 2.6. Most likely mechanisms how metals interact with cement-based systems

In order to accelerate setting and hardening of cement-based systems containing heavy metals, the additions of admixtures to cement have been examined. Choon-Keun and Park (**82**) compared setting time, surface area, compressive strength and leaching behaviour of two types of modified cement (SS1, SS2) against plain cement. One of the modified cements (SS1) included 20% of cement replaced with the admixture CKD. The admixture CKD possessed a higher alkali sulfate concentration and twice higher surface area than cement. The second modified cement (SS2) included 15% of admixture CKD and 10% of admixture QSA. The admixture QSA was mainly calcium sulphoaluminate and anhydrite. Heavy metals were added to the three cementitious systems (SS1, SS2 and plain cement) by using either pure compounds of Cd, Pb and Cr or a waste containing Cd, Pb and Cr. Waste used was from the steel industry. Results for using pure heavy metals addition and that for the waste were similar. Compared to plain cement, the initial and final setting times for SS1 were 1 and

2 hours lower respectively, and those for SS2 were 3 and 4 hours lower respectively. The reduction of setting time for SS1 and SS2 is due to the formation of ettringite resulting from the high content of calcium sulphoaluminate and anhydrite in QSA and the presence of alkali sulfates and high surface area of CKD.

2.4.6 Migration of Metals Contained in Cement-Based Systems into the Environment

Waste bound in cement-based systems may be subject to further reactions in contact with the natural environment. Long-term assessments of these systems have proved that heavy metals, contained in a cement matrix, can be leached into soil and surface and ground water. Water or flowing solutions may cause the migration of metals contained in cement-based systems to the environment. The mobility of metals from solid phases to liquid depends on the intrinsic nature of the metal, the waste-cement-based system, and the aqueous solution. The different parameters involved in the mobilisation of heavy metals contained in cement-based materials can be summarised as follows:

1. *Type of bond between metals and cement matrix.* In general, metals chemically bound with the cement matrix are better immobilised than those only physically bound (**19**). The possible mechanisms involved in the immobilisation of metals were discussed in detail in section 2.4.5. The dissolution of Hg, which precipitated as HgO (**96**) in cement-based systems, is easier than those heavy metals (e.g. Cr, Pb, etc), which may be incorporated into lattice structure and/or adsorbed onto surface of hydrates. The immobilisation of metals also depends on the oxidation state of the element, Glasser (**79**) reported that Cr(III) is better immobilised than Cr(VI) despite both being very soluble in cement-based systems. This effect can explain the better immobilisation of cation ions than anionic species in cement-based systems due to the higher competency of anionic species for sorption sites.

2. *Dissolution of cement matrix.* The dissolution of the cement matrix is influenced in part by the physical properties of the cement matrix, such as permeability and porosity and by the presence of aggressive aqueous agents in contact with cement-based systems. High permeability and porosity facilitate flow of water through the cement matrix thereby increasing dissolution of metals. In cement-based systems, containing either slag or fly ash, a reduction in permeability due to more efficient packing has been observed. The more efficient packing tends to limit the mobility of metals (**79**). However, since the addition of blending agents normally reduces the pH in pore water, the leaching behaviour of certain heavy metals (e.g. Cu, Zn, and Pb) can be enhanced (**83**) due to the higher solubility of these elements as pH

decreases. The ageing of the cement-based system containing metals also influences the mobility of metals into the environment. Once reactions between metals and the cement matrix have been completed, the mobility of heavy metal ions slows (**79**).

3. Solubility of metal compounds. In cement-based systems, metal hydroxides and different metal hydrates are commonly found. The solubility of these different forms of metals is strongly dependent on pH values of the pore water and surroundings (**102**). In general, as the pH decreases the solubility of metals increases.
4. Complexation reaction. The presence of specific organic complexants in the aqueous solution can influence the dissolution of certain heavy metals (e.g. Cu). The reaction consists of movement of heavy metals from solid phases to aqueous phases by forming metal complexes. The solubility and biological effects of metal complexes are different for each metal examined (**19**).

2.4.7 Fixation and Leachability of Sulfates and Chlorides in Cement-based Systems

The presence of gypsum or other sulfate compounds is required to retard the hydration reaction of C_3A, as mentioned previously (section 2.4.1). However, either an excess or lack of SO_4^{2-} changes the chemical composition of the hydrates and the physical, mechanical and durability properties of cement-based systems. An excess of SO_4^{2-} causes a false set due to a rapid formation of ettringite, thereby, reducing the formation of calcium silicate hydrates. On the other hand, in the absence or lack of SO_4^{2-}, calcium aluminates hydrates, C_3AH_6 are formed rapidly which causes a reduction in the formation of C-S-H phases. In addition, the lack of SO_4^{2-} may leave anhydrous C_3A which can react with external SO_4^{2-} ions forming ettringite once cement-based systems are in a hardened state. Thus, the concentration of soluble sulfates contained in waste is an important parameter to consider when the utilisation of wastes is examined.

The presence of chlorides in cement-based systems has special interest in reinforced concrete. Chloride contents must be kept low to avoid corrosion of steel that disrupts the concrete. Apart from the danger of corrosion of steel, chlorides may absorb moisture from air and cause efflorescence (**33**). Efflorescence is associated with two aspects; one leaching of lime compounds on the surface of concrete and other depositions of white salts from aggregates on the surface of concrete (**103**).

The main form of binding the sulfates and chlorides ions is by the reaction with C_3A to form ettringite and calcium monochloroaluminate, known as Friedel's salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$), respectively (**104**). A similar reaction with C_4AF results in

calcium chloroferrite. Auer et. al. (**105**) studied the hydration of MSWI fly ash with a reactive calcium aluminate cement, $C_{12}A_7/C_3A$. They reported that soluble sulfates contained in MSWI fly ash were rapidly fixed due to formation of ettringite. Once the fixation of sulfates in ettringite had been completed, calcium monochloroaluminate started to crystallise by reaction of the remaining calcium aluminates with Cl^{1-} ions contained in MSWI fly ash. The presence of high concentrations of Cl^{1-} did not seem to influence the formation of ettringite. Theoretically, the hydration reaction can be formulated as follows:

$$C_{12}A_7 / C_3A + CaSO_4 2H_2O + NaCl + KCl \rightarrow \qquad \textbf{Reaction 2.16}$$

$$3CaOAl_2O_3 3CaSO_4 32H_2O + 3CaOAl_2O_3CaCl_2 10H_2O + K^+ + Na^+ + Al_2O_3 3H_2O + Cl^- + OH^-$$

They found that both crystalline forms of ettringite and Friedel's salt were able to incorporate heavy metals, especially ettringite, The presence of chlorides in ettringite was not detected.

Alba et. al. (**106**) studied the immobilisation of chlorides, sulfates and heavy metals using different MSWI fly ashes that were stabilised with cement. They reported that sulfates and heavy metals were well immobilised in the cement-based systems, whereas chlorides were partially retained as Friedel's salt. In addition, they observed an increase in leachability of heavy metals and sulfates as carbonation continued. The carbonation decreases the pH and then the metal ions can be dissolved at low pH values. The increase in sulfate ions in aqueous solution was due to the carbonation of ettringite that produces gypsum and sulfate ions pass to solution.

Dumitru et. al. (**107**) examined the influence of barium (Ba) on the hydration of cement-based systems. They reported that, in the absence of gypsum, $BaCO_3$ delayed the hydration of C_3A due to formation of hydrated calcium-barium carboaluminates. However, in the presence of gypsum or other sulfates, the hydration of C_3A was accelerated, whereas the formation of ettringite was inhibited. Ba^{2+} reacted with SO_4^{2-} ions forming high amounts of $BaSO_4$ which is a highly insoluble salt. This reaction reduced significantly the concentration of sulfates in solution, and consequently ettringite could not be formed. $BaCO_3$ would act as a bonding agent of sulfates either coming from the external medium or from the addition of waste, which may contain high contents of sulfates.

2.5 MECHANICAL, PHYSICAL AND DURABILITY PROPERTIES OF CEMENT-BASED SYSTEMS

2.5.1 Compressive Strength

Compressive strength at 28 days is considered to be the most common property used to define the quality of concrete. Strength is closely related to the degree of hydration and structure of the hardened concrete. The structure of hardened concrete also influences the physical and durability properties. Strength of concrete materials depends on the cohesion of cement paste, the bond between the paste and aggregates (**39**). Compressive strength values are mainly dependent on water content, composition and content of cement, type and content of aggregates and curing method.

The effect of cement replacement materials, such as slag, fly ash and silica fume on compressive strength of concrete or paste materials has been widely discussed (**73,76-79**). Factors influencing strength in composite cement-based systems are mainly chemical composition, level of replacement and fineness of replacement materials as well as the type and length of curing (**76-79**). The content of SiO_2, CaO, free CaO and sulfate in composite cement-based systems have a strong influence on the level of cement replacement and on the short and long terms strength. The higher reactive SiO_2 content in slag compared to fly ash, coupled with higher CaO content, enables higher cement replacement levels to be used (**108**). Replacement materials containing high CaO content show higher early compressive strength than waste with low CaO content. This effect is attributed to the higher contribution of cementitious properties versus pozzolanic characteristics (**109**). Fineness is an important factor that can affect the rate of hydration reaction and the homogeneity of the hardened material. Studies on fly ash showed that the increase in the specific surface area of fly ash permits high replacement levels and increases long-term strength, which can be equal to or greater than the reference mix (**110**). Studies on the influence of the type of curing on slag and fly ash cements have proved that the compressive strength of a cement matrix containing either slag or fly ash is more sensitive to different curing regimes than plain cement (**111,112**).

In general, the replacement of cement with either slag or fly ash, which exhibit pozzolanic properties, reduce early strength and increase long-term strength compared with plain cement (**108, 113**). At present, data on the compressive strength of cement-based systems containing Municipal Solid Waste Incineration Bottom Ash (MSWI-BA)

as cement replacement are limited compared with those for slag and fly ash. Most of the current literature focuses on the use of MSWI-BA as aggregate.

The lower homogeneity of MSWI-BA compared with natural aggregates coupled with cracking and swelling phenomena due to formation of H_2, are mainly the reasons for reducing the strength of concrete containing MSWI-BA as aggregate (**114-116**). The formation of H_2 occurs with the reaction of aluminium with cement, as shown in Reaction 2.17.

$$2Al + Ca(OH)_2 + 2H_2O \rightarrow Ca(AlO_2)_2 + 3H_2 \qquad \textbf{Reaction 2.17}$$

Strength of mortar containing MSWI-BA as cement replacement depends on the parameters discussed above for slag and fly ash (e.g. contents of reactive SiO_2 and CaO) and on the concentrations of metals, chlorides and sulfates. The interactions of metals, chlorides and sulfates with cement and aggregates have been discussed in sections 2.4.4 to 2.4.7. Thus, strength can be reduced as a consequence of the coating effect caused by deposition of some metals on the surface of cement grains and hydration products. The deposition of metals causes a reduction of both short and long term compressive strength (**96- 100, 117**). To reduce the effect of metals on compressive strength, the addition of different admixtures has been investigated. Choon-Park (**82**) reported that the compressive strength of cement-based systems containing metals could be improved when an admixture, SS2, was added which contained high contents of C_3A and sulfates. High levels of C_3A and sulfates cause an increase in the formation of ettringite which bonds with the heavy metals, thereby, reducing the coating of heavy metals on the surface of the cement grains. This increases the rate of hydration and subsequently increases the strength. However, when other admixture, SS1, which contained high content of alkalis and sulfates, was added only the early strength was higher compared with the control mix, but the long-term strength was decreased.

Filipponi et al. (**117**) investigated the possible pozzolanic activity and compressive strength of a fraction of MSWI-BA whose grain diameter was below 150μm. They found that replacing cement with MSWI-BA reduced the amount of $Ca(OH)_2$ in hydrates compared with a reference mix (100% cement). This means that Portlandite is consumed by additional reactions such as pozzolanic reaction. However, those mixes with cement replacement levels equal to or greater than 30% did not exhibit a reduction in the concentration of $Ca(OH)_2$. In addition, for all levels of replacements examined, compressive strength values were lower than for the control mixes.

2.5.2 Drying Shrinkage

The removal of water from the surface of hydrated materials (e.g. paste or concrete) exposed to natural drying in a controlled humid environment is known as drying shrinkage. If materials are subject to a drying process, the free water that is evaporated first causes little or no shrinkage. As drying continues, adsorbed water from the surface of gel particles, which was surrounded by free water, is removed and gel particles move together by a distance similar to the thickness of the adsorbed water layer, thereby, causing a shrinking effect. It is also possible that a part of the shrinkage is related to the removal of intracrystalline water from calcium silicate and sulfoaluminate hydrates. A part of the movement produced by drying shrinkage is irreversible due to the formation of additional bonds within gel particles (**118**).

Some of the main factors influencing drying shrinkage include water/cement (w/c) ratio, cement content, aggregate content and the type of aggregates. Increasing w/c ratio increases shrinkage because w/c ratio determines the amount of water in the system and the rate at which water can move toward the surface of the specimen (**118**). Increasing aggregate content exerts a positive influence on drying shrinkage. Since drying shrinkage is closely related to the surface area of hydrated material, the introduction of aggregates causes a decrease in shrinkage as result of the reduction of hydrated surface areas. For the same reason large size of aggregates will reduce drying shrinkage. Figure 2.7-(a) shows the influence of w/b ratio and aggregate content on shrinkage (**119**), whereas Figure 2.7-(b) shows the combined influence of cement and water contents and w/b ratio on shrinkage (**120**). At a constant w/c ratio, shrinkage increases with an increase in the cement content as result of the increase in volume of hydrated surface which is liable to shrinkage. However for constant water content, shrinkage slightly decreases as cement content increases. This is due to a decrease in the w/c ratio.

Apart from aggregate content, the restraining effect of the aggregates on shrinkage must be considered due to the elastic modulus of aggregates. Aggregates that offer high restraint to the potential shrinkage of cement paste will decrease shrinkage whereas aggregates, such as lightweight aggregates, with low module of elasticity allow higher shrinkage (**118**).

Others factors which may affect drying shrinkage are the chemical composition of cement, type of curing and storage conditions. The chemical composition of cement is believed not to affect shrinkage except for cements deficient in gypsum. These cements give an increase in shrinkage due to the different structure of hydrated paste, gel/space ratio and strength (**118**). The relative humidity of the medium greatly affects

the magnitude of shrinkage. Concrete placed in dry air conditions shrinks but it swells in water or air with a relative humidity of 100% (**121**). Prolonged moist curing delays the advent of shrinkage, but in general the length of the curing period before exposure to drying does not affect significantly the magnitude of shrinkage (**118**).

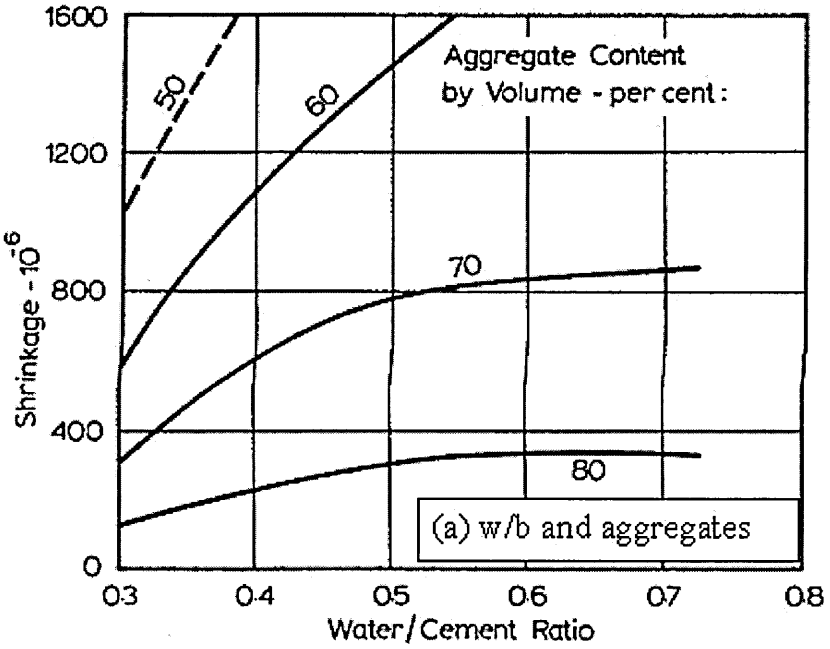


Figure 2.7-a. Influence of w/c Ratio and Aggregates Content on Shrinkage(119)

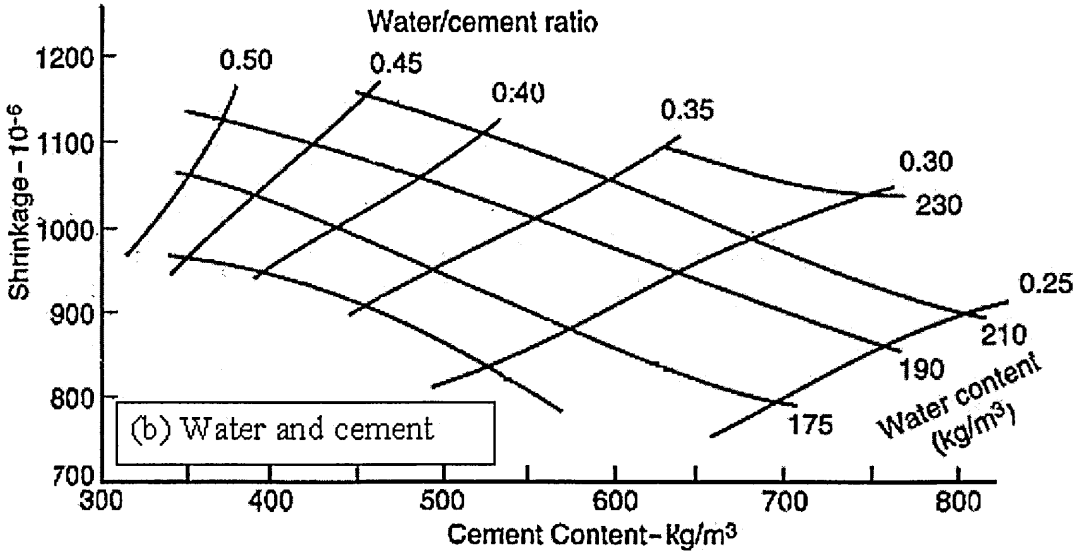


Figure 2.8-b. Influence of cement and water contents couple with w/c ratio on Shrinkage (120)

A guide of shrinkage values at six months for concrete made with constant w/c=0.5 and aggregate/cement ratios of 3, 4, 5, 6 and 7 stored at a temperature of 21°C and 50% RH are 1200μs, 850μs, 600μs, 400μs and 300μs respectively (**118**).

In the current literature there is little information about effects of using MSWI-BA on drying shrinkage. However, drying shrinkage for concrete containing either fly ash or slag is well documented in the literature. Replacement of cement with fly ash does not affect the drying shrinkage. Even concretes containing high contents, up to 50% of replacement materials, exhibit a drying shrinkage similar to or lower than plain concretes (**110**). Concrete made with a high proportion of fly ash may have higher drying shrinkage at early ages due to the retardation effect caused by pozzolanic materials. However, long-term shrinkage can be similar to the control mix (**110**). The effects of replacing cement with slag materials on drying shrinkage are not clearly defined. While some experimental results have shown that slag, in binders, does not greatly affect drying shrinkage (**113**), others have indicated an increase of drying shrinkage with increasing slag content (**122-124**). This discrepancy of results may be attributed to the different experimental techniques and physical and chemical properties of slag used during each experimental work.

The high absorption affinity of MSWI-BA can be used to predict a high drying shrinkage, when it is used as aggregate replacement. Absorption is associated with the elastic properties of aggregates, thereby affecting with drying shrinkage (**118**). Wainwright et al. (**58**) evaluated the shrinking performance of concrete containing 50% of natural aggregates replaced with an untreated MSWI-BA (with diameter 600μm<∅<6mm). They observed higher drying shrinkage for concrete containing MSWI bottom ash than the control mixes. A high drying shrinkage was also observed for concretes containing a synthetic fraction of MSWI-BA whose particle diameters were below 600μm.

2.5.3 Porosity

Porosity or total pore volume of a solid material is a measure of the volume of voids with respect to the total volume. Porosity and structure of pores (e.g. diameter, shape) of plain and composite cement-based systems have been extensively studied due to their influence on physical, mechanical and durability properties of these systems (**125-129**). In order to describe and evaluate pore structure of materials, different classifications of pores, as a function of diameter, have been suggested.

In cement paste, pores are commonly divided into gel pores and capillary pores (**130**); gel pores are interstitial voids within the gel particles, C-S-H, and lie generally below 0.01μm; capillary pores are originated by the incomplete filling of space between former cement grains and new hydration products. Capillary pores have a diameter ranging approximately from 0.01μm to 5μm (**131**). Nevertheless, a clear distinction

between the pore diameters of gel and capillary pores can not be made. The continued hydration of cement paste leads to an increase in gel pores and a decrease in capillary pores due to the formation of hydrates and the filling of open pores by hydration products respectively (**127,131**). For cement paste, the total porosity typically lies within the range 16-24% (**79**).

In mortar or concrete, the porosity and pore size distribution are somewhat different from those for cement paste because of the influence of aggregates (**132**). Feldman (**133**) reported a significant difference in the pore size distribution of mortar as a function of sand/cement ratio due to the interfacial effect. As the sand/cement ratio increase, the amount of interface per volume of specimen should increase and large pores may be formed around the sand grains. In addition other factors may contribute to this phenomenon. Thus, during hydration $Ca(OH)_2$ is preferentially deposited at the interfacial zone around aggregates. Large $Ca(OH)_2$ crystals may develop in this zone after a few days. This modified form of deposition of products is likely the cause of the changes in pore size distributions. The $Ca(OH)_2$ reduction in the matrix due to its deposition at interface can reduce permeability of the body and access to cement grain by H_2O. This may results in limited hydration compared with mixes without sand and can account for increased porosity. In addition, Winslow and Liu (**134**) found that, with the same paste composition and at the same degree of hydration the presence of coarse aggregates results in an increase in porosity. The difference in porosity between concrete and paste, at same the w/c ratio, increases with the progress of hydration and arises from the presence of large pores in concrete compared with small pores in the paste. However, well cured concrete made with low w/c ratio and not air entrained should contain some pores with diameter greater than 1μm.

In practice, pores with diameters ranging between 0.01-1μm dominate transport and permeation properties because finer pores present a high frictional resistance to flow (**77,79**).

Most experimental studies have tried to find a correlation between total porosity and pore size distribution with compressive strength. Several equations have been proposed to express the relationship between compressive strength and porosity (**135-140**). Although the different equations and relationships may vary, it is agreed that strength increases as porosity decreases. In addition, it has been suggested that strength is governed more by total pore volume rather than pore size distribution (**131,141,142**). Therefore, strength of concrete is influenced by the total volume of all voids such as entrapped air, capillary pores, gel pores and entrained air (**132**). In

addition, it has been observed that at a given porosity, a high proportion of small pores lead to a higher strength (**132**).

Durability properties are governed by the ability of water or aggressive ions to pass through the body of materials. The transport of fluids through materials, commonly referred to permeability, is obviously associated with the pore system, which can consequently be related to the pore size distribution. The pores that affect the permeability have to be continuous and with a diameter of at least 0.120 or 0.160μm (**143**). If the porosity is high and pores are discontinuous (e.g. aggregate pores, air voids) or otherwise ineffective with respect to transport, the permeability is low. Hence, reducing permeability rather than total porosity can restrict the flow of solutions through the hydrated material, thereby improving durability performance (**144-146**).

An important physical action of waste such us fly ash and slag arises from their characteristic geometry. The packing of cement-based systems containing fly ash or slag blends more efficiently filling space than would each of the constituents on its own (**77**). The addition of fly ash or slag may not greatly affect the total porosity but can decrease the permeability due to the reduction in the connectivity between pores. Connectivity of pores can be reduced as a result of the pore refinement or the discontinuity of pore structure. Pore refinement develops with the increase in time .This leads to a decrease in permeability (**79**).

2.5.4 Sulfate Resistance

Physical (e.g. high temperature), mechanical (e.g. impact) and chemical attacks can cause deterioration and loss of durability of cement-based systems. Chemical attacks can be internal (e.g. alkali-silica reaction) and external (e.g. effect of acids, chlorides, sulfates or carbon dioxide). One of the common causes of deterioration of concrete is due to the external attack of sulfates from soil and natural or contaminant ground waters. In particular, Na_2SO_4 and $MgSO_4$ solutions can cause higher degree of deterioration of concrete structures than $CaSO_4$ solutions, due the low solubility of the latter and also possible decalcification of C-S-H gel caused by $MgSO_4$ (**143**). Sulfate resistance of concrete structures needs to be considered explicitly at the design stage, to ensure that concrete structures can reach their intended service life (**143**).

In general, sulfate attack of hardened cement-based systems leads to the conversion of primary hydration products (ex. CH, C_3A and C-S-H) to new products such as ettringite, thaumasite and gypsum. The formation of these new products produces disruptive expansion, cracking, loss of strength and ultimately disintegration (**84**). The

damage usually starts at edges and corners and is followed by progressive cracking (**143**).

There is a controversy about the exact mechanism that causes the expansion resulting from sulfate attack (**147, 148**). Thus, numerous mechanisms have been proposed to explain such expansion. The reactions between sulfate solutions and hydrated products can be formulated as follows (**143**):

Sodium sulfate reacts with $Ca(OH)_2$, (CH), and deposits gypsum as shown in reaction 2.18. Softening of concrete surface has been attributed to the effect of gypsum (**149**).

$$Ca(OH)_2 + Na_2SO_4.10H_2O \rightarrow CaSO_4.2H_2O + 2NaOH + 8H_2O \quad \textbf{Reaction 2.18}$$

Na_2SO_4 also attacks the calcium aluminate hydrate (C-A-H) phases to form ettringite, as shown in reaction 2.19. The expansion observed as consequence of the sulfate attack is attributed to the formation of ettringite (**149**).

$$2(3CaO.Al_2O_3.12H_2O) + 3(Na_2SO_4.10H_2O) \rightarrow 3CaO.Al_2O_3.3CaSO_4.31H_2O + 2Al(OH)_3 + 6NaOH + 17H_2O \quad \textbf{Reaction 2.19}$$

Magnesium sulfate not only attacks the CH and C-A-H phases but also the C-S-H phases, this is shown in reaction 2.20. Since $MgSO_4$ attacks C-S-H as well its effect is more aggressive than other sulfate attacks. Portlandite is replaced in presence of $MgSO_4$ with brucite ($Mg(OH)_2$) and gypsum. This results in a drop in pH (brucite has very low solubility) in contrast with Na_2SO_4 that causes an increase in pH. At low pH, C-S-H becomes instable and reacts with $MgSO_4$ to form M-S-H and gypsum, but the former is non-cementitious material.

$$3CaO.2SiO_2.aq + MgSO_4.7H_2O \rightarrow CaSO_4.2H_2O + Mg(OH)_2 + SiO_2.aq \quad \textbf{Reaction 2.20}$$

Calcium sulfate attacks only the C-A-H and ettringite is formed, as shown for Na_2SO_4 in reactions 2.19.

In addition to the formation of gypsum and ettringite as a consequence of sulfate exposure, thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$) can also be formed. The formation of thaumasite occurs under specific conditions, such as low temperature (0-5°C), presence of CO_2 or CO_3^{1-} and high pH about 12.5 (**150**). Recent evidence, however, has shown that thaumasite can be formed at temperatures higher than 5°C only in very small amounts (**149**).

The susceptibility of cement-based systems to sulfate attack depends on both physical and chemical factors:

a) *Physical factors:*

The influence of physical factors is clearly understood. All adverse fluid attacks depend on the transport of fluids through the body of concrete materials. Permeability is the commonly accepted term for overall movement of fluids through materials (**143**). Larbi (**151**) observed that permeability in concrete is mainly controlled by the bulk of the hardened cement paste because that is the only continuous phases in concrete. In fact, the permeability of concrete can be reduced compared with the hardened paste due to the presence of aggregates. Aggregates inhibit the flow of fluid through concrete.

b) Chemical factors

A reduction in the content of the constituents (e.g. CH and C-A-H) that contribute to the sulfate attack may enhance the sulfate resistance of the systems. In general, cements with low C_3A content, sulfate-resisting Portland cement (SEPC) are used to enhance the sulfate resistance of concrete. Nevertheless, a reduction in the amount of C_3A in the cement-based system to increase sulfate resistance is not always positive. Thus, Santhanam et al (**152**) reported that decreasing the C_3A content might improve sulfate resistance when exposed to sodium sulfate. However, when exposed to magnesium sulfate the use of low C_3A cements may be inadequate because the C-S-H can be directly attacked. Additionally the formation of thaumasite is not inhibited when binder with low C_3A content are used.

Furthermore, the use of cement with low C_3S content and pozzolanas can improve the sulfate resistance of concrete as a consequence of the reduction in the amount of CH produced at the early stage of hydration. Irassar et al (**153**) observed that the sulfate resistance of low C_3A Portland cement was relatively poor when cement had a high C_3S/C_2S ratio. This was attributed to the initial formation of gypsum due to the reaction of CH with sulfates at the early stage of the attack and the formation of ettringite from ferroaluminate hydrates at the later stage of the sulfate attack.

Partial replacement of cement by pozzolanic materials (e.g fly ash, ground brick, slag) has been widely investigated in order to reduce the external sulfate attack (**147,148,154**). Pozzolans can not only reduce the content of CH and thereby the gypsum formation, but also reduce porosity and permeability as a result of pore refinement and block pore effects.

Since, utilization of pozzolans is a well-established method to enhance sulfate resistance of cement-based systems; this programme of research has examined the effect of MSWI-BA on sulfate resistance of mortar specimens. Studies on MSWI-BA

used as a suppressor of sulfate attack have not been published yet due to the lack of li on the use of MSWI-BA as a pozzolan.

2.5.5 Leaching Behaviour

Leaching toxic metals and salts (e.g. sulfates and chlorides) is the most basic mechanism how cement-based systems containing waste materials may contaminate into the environment (**155,156**). Determination of leachate concentrations are used commonly as compliance criteria to evaluate the toxicity of wastes. The study of the leaching behaviour, apart from assessing the environmental quality, can be used as a tool for examining the binding mechanisms and durability of properties of composite cement-based systems (**92,93,101**).

Leaching behaviour of cement-based systems containing wastes has been studied widely as a result of the extensive use of cement systems to immobilise metals or other contaminants (**79,97,100**). A summary of binding mechanisms and influence of metals, sulfates and chlorides on cement-based systems properties have been discussed in detail in sections 2.4.5, 2.4.6 and 2.4.7. This summary can be used to explain the leaching behaviour of cement-based systems containing MIWI-BA.

The existing published work on leaching behaviour of bound MSWI-BA is based on using batch leaching procedures (**157,158**). In general, these procedures are designed to simulate aggressive scenarios for granular material. The leachate concentrations obtained from this batch leaching test can not be compared realistically with field situation.

2.6 CONCLUSIONS

Chapter 2 includes a review of two main areas. One area reviews the role of MSWI-BA within waste management schemes, the chemical, physical, leaching properties and current utilisation of MSWI-BA; the other area examines the chemistry, mechanical, physical and durability properties of plain and composite cement-based systems. The review of MSWI-BA waste management schemes indicated an increase in the generation of MSWI-BA and a significant reduction in the amount of MSWI-BA sent to landfill sites. Therefore, there is a need to investigate and find a use for MSWI-BA.

The examination of physical, chemical properties environmental and current utilisation of MSWI-BA suggested that this ash can be used in construction, especially as aggregate. In addition, the engineering and environmental properties of MSWI-BA can be improved significantly when fine particles (e.g. grain diameter below 2mm) are

rejected due to their high porosity and possible toxicity. Having identified the need to improve the uses of the fine fraction of MSWI-BA, this programme of research investigates new possible uses of the fraction of MSWI-BA with particle diameter below 2.36mm.

The examination of the chemistry of cement-based systems was focussed on explaining the main reactions (e.g. hydration, alkali-silica, pozzolanic) that may occur in plain and composite cement-based systems. This examination is used to understand and explain the mechanical, physical, durability and leaching properties of such systems. Especially, compressive strength, drying shrinkage, porosity, sulfate resistance and leaching behaviour of plain and composite cement-based systems have been reviewed in more detail. Because there is a lack of published information on MSWI-BA used as a partial replacement of cement, the examination of composite cement-based systems has concentrated on explaining effects that were observed in well- known wastes such us fly ash and by-products such us slag.

The following chapter (Chapter 3) consists of a description of materials, instruments, techniques and test methods that have been used throughout the experimental programme. Specific methodology that may be required for particular tests is given in the corresponding chapter.

2.7 REFERENCES

1 Environmental Agency. "Waste Minimisation and the Environmental Agency". DO40APRLR. 1999

2 Sakai, Sawell S.E. and Chandler A.J. "World Trends in Municipal Solid Waste Management". Waste Management, Vol 16, Nos 5/6, pp 341-350. 1996

3 Sawel S.E., Hetherington S.A. and Chandler A.J. "An Overview of Municipal Solid Waste Management in Canada". Waste Management, Vol 16, Nos 5/6 pp351-359. 1996

4 EPA "International Solid Waste Practices". Review 1997 Http://www.epa.gov/epaoswer/non-hw/muncpl/factbook/internet. Visited 19 Feb.2002

5 Péra J. and Ambroise J. "Incineration of Wastes and the Environment". Proceedings of the International Symposium of Sustainable Construction: Use of Incinerator Ash. Edited by R. K Dhir Tom D. Dyer and K. and Kevin A. Paine. Dundee (UK). 2000

6 Environment Agency. Visited 20 April 2000

http://www.environment-agency.gov.uk/epns/waste/index.htm#Overview

7 Gilbert M. "Introduction to Environmental Engineering and Science". Masters. 2nd Ed. Section 9.9. 1998

8 Waste Watch Wasteline. "Energy form waste". 1999

9 The World Resource Foundation. "Energy from waste". October 1996

10 http://www.caddet.co.uk/re/html/body_298art3.htm. Visited April 2000

11 http://www.gvrd.bc.ca/waste/incinfs.pdf. Visited Agust 2000

12 Braymand S., Clastres P, and Pellequer A. "Mineralogical Hydraulic and Mechanical Characterisation of Solidified and Stabilised MSWI Fly Ash. Contribution of Blast Furnace Slag". Waste Materials in Construction. Ed. Woolley G.R., Goumans J.J. J. M. and Wainwright P.J. Elsevier Science 2000

13 Mulder E. "Pre-Treatment of MSWI Fly Ash for Useful Application". Waste Management, Vol. 16, Nos. 1-3 pp181-184. 1996

14 Cheong, M., Tay, H-K., and Show, J-H."Utilisation of MSWI fly ash as innovative civil engineering materials". Proceedings of the International Symposium of Sustainable Construction: Use of Incinerator Ash. Edited by R. K Dhir Tom D. Dyer and K. and Kevin A. Paine. Dundee (UK). 2000

15 Halliday J. E., Dyer T. D. and Dhir R. K. "Use of Incinerator Fly Ash as Pozzolanic Activator". Proceedings of the International Symposium of Sustainable Construction: Use

of Incinerator Ash. Edited by R. K Dhir Tom D. Dyer and K. and Kevin A. Paine. Dundee (UK). 2000

16 Baur I., Ludwig C.H. and Johnson C.A. "Leaching Processes in Cement-Stabilised Municipal Incinerator Air Pollution Control Residues". Waste Materials in Construction. Ed. Woolley, G.R., Goumans. J.J. J. M. and Wainwright, P.J. Elsevier Science 2000

17 European Commission. EEC 89/368 Directive. December 1996

18 Sawell S.E., Chandler A.J., Eighmy T.T., Hartlen J., Hjeelmar O., Kosson D., Van der Sloot H.A. and Vehlow J. "An International Perspective on the Characterisation and Management of Residues from Municipal Solid Waste". Biomes and Bio-energy, Vol.9, Nos 1-5, pp 377-386. 1995

19 Johnson C.A. "A Geochemical Perspective on the Factors that Control Long-Term Emission from Municipal Solid Waste Incinerator". Proceedings of International Symposium "Use of Incinerator ash". Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

20 Waste Watch Wasteline. "*Legislation Affecting Recycling*". 1999

21 Author: Ian Jones 20-nov-2001. http://www.environment-agency.gov.uk/news/202518?lang=_e&region=&projectstatus=&theme=&subject=&searchfor=municipal+solid+waste&topic=&area=&month= 19 February 2002.

22 Author: Ian Jones -Dec-2001 http://www.environment-agency.gov.uk/news/214030?lang=_e&region=&projectstatus=&theme=&subject=&searchfor=municipal+solid+waste&topic=&area=&month= 19 February 2002.

23 Seliger A. and Schmidt V. "The ABB Dry Ash Concept : InRec™ ". Waste Material in Construction: Putting Theory into Practice. Elsevier Science. 1997

24 Pfrang-Stotz G. and Reichelt J. "Municipal Solid Waste Incinerator Bottom Ash: Characteristics and the Use in Road Construction". Proceedings of International Symposium "Use of Incinerator Ash". Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

25 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste Incinerator Residues". Chapter 2; Municipal Solid Waste. Studies in Environmental Science 67. Elsevier 1997

26 Long Island Region Planning Board (LIRPB). "The potential for Use of waste Energy Facility Ash". Final Report, LIRPB/NYSERDA. 1993

27 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste

Incinerator Residues". Chapter 12: Physical Aspect of Leaching. Studies in Environmental Science 67. Elsevier Chapter 21997

28 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste Incinerator Residues". Chapter 9: Bottom Ash. Studies in Environmental Science 67. Elsevier 1997

29 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste Incinerator Residues". Chapter 7; Characterisation Methodologies. Studies in Environmental Science 67. Elsevier. 1997

30 Veabrin. Veabrin Kwaliteitskontrole van AVI-Slakken 87-88. RAP-305/JJS avd. 1988

31 Hartlen J. and Rogbeck J. "Sorted Incinerator Slag Used as Fill Material". International Conference on Municipal Waste Combustion. Proceeding, Vol. 1. Florida, 1989

32 Eighmy T.T., Domingo D, Stampfli D., Krzanowsi J. and Eusden J.D. "The Nature of Elements in Combustion Residues and their Stabilised Products". pp 541-575. In Proceedings of 1992 Incineration Conference. Albuquerque, New Mexico, 1992

33 Neville A.M. Properties of Concrete. Chapter 3: Properties of Aggregates. Ed. Longman Group Limited, Fourth and Final Edition. 1995

34 BS 3797.1990. Specification for Lightweight Aggregates for Masonry Units and Structural Concrete

35 Eighmy T.T., Gress D., Zhang X., Tarr S. and Whitehead I. "Bottom Ash Utilisation and Evaluation for the Concord, New Hampshire Waste-to-Energy Facility". Environmental Research Group. Interim Report, UNH Durham, NH 1992

36 Pavasars I. "Comparison of Organic matter in Bottom ash from MSWI." Waste Materials in Construction. Ed. Woolley G.R., Goumans J.J.J.M. and Wainwright P.J. Elsevier Science 2000

37 BS 3892: Part 1:1997. Pulverised-Fuel Ash. Part 1. Specification for Pulverised-Fuel Ash for Use with Portland Cement

38 BS 882. 1992. Specification for aggregates from natural resources for concrete

39 Neville A. M. "Properties of Concrete". Chapter 1; Portland Cement. Ed. Longman Group Limited, fourth and Final edition. 1995

40 Stämpfly. Personal communication. 1992

41 Johnson C.A., Kersten M., Ziegler F. and Moor C. "Leaching Behaviour and Solubility Controlling Solid Phases of Heavy Metal in Municipal Solid Waste Incinerator Ash". Waste Management. Vol.16, Nos. 1-3 , pp 129-134.1996

42 Sawel S.E. and Constable T.W. "The National Incinerator Testing and Evaluation Program. A Summary of the Characterisation and Treatment Studies on Residues from Municipal Solid Waste Incineration". Environment Canada Publication No. EPS 3/UP/8, Ottawa, Canada 1993

43 Stämpfli D., Belivi H., Fontanive R. and. Bacchini P. "Reactions of Bottom Ash from Municipal Solid Waste Incinerators and Construction Waste Samples with Water". EAWAG/AWS, project 3335, Dubendorf, Switzerland 1990

44 Vehlow J., Pfrang-Stotz G. and Scheneider J. "Restoffe-Charakterisierrung, Behandlung, Verwertug." In Simposium 25 Jahre LIT 5Jahre TAMARA, Forschung und Entwicklung in Kernforschungszentrum Karlsruhe zur Hausmüllverbrennung Kfk, Karlsruhe, Germany, p 124 .1992

45 Kirby, C.S. and Rimsstidt D.J. "Mineralogical and Surface Properties of Municipal Solid Waste Ash". Environmental Science Technology. Nos 27; pp 652-660. 1993

46 Eighmy T.T., Eusden Jr J.D., Marsella K., Hogan J., Domingo D., Krzanowsi J.E. and Stampfli D. "Particle Petrogenisis and Specification of Elements in MSW Incineration Bottom Ash". Environmental Aspects of Construction with Waste Materials. Edited by Goumons J.J.JR., van der Sloot H.A. and Albers T.H. G. Elsevier Science pp 111. 1994

47 Meima J.A., van der Weijden R.D., Eighmy T.T. and Comans R.N.J. "Carbonation Process in Municipal Solid Incinerator Bottom ash and their Effect on the Leaching of Copper and Molybdenum". Applied Geochemistry article in press. 2001

48 Commans R.N.J., Meima J.A. and Geelhoed P.A. "Reduction of Contaminant leaching from MSWI Bottom Ash by Addition of Sorbing Components". Waste Management No 20, pp 125-133. 2000

49 Meima J.A. and Commans R.N.J. "The Leaching of Trace Elements from MSWI Bottom Ash at Different Stages of Weathering". Applied Geochemistry No 14 pp 159-171. 1999

50 Hartlen J. and Elander P. "Residues from Waste Incineration-Chemical and Physical Properties". Swedish Geotechnical Institute report SGI Varia 172. Linkoping, Sweden 1986

51 Hartlen J. and Lundgren T. "Utilisation of Incinerator Bottom Ash; Legal, Environmental and Engineering Aspects" In Waste Materials in Construction. Edited by Goumans J.J.J.R., Van der Sloot H.A. and Aalbers T.G.. Elsevier Scientific Publishers B.V., Amsterdam, p 207. 1991

52 Zevenbergen C. "Weathering as a Process to Control the Release of Toxic Constituents from MSW Bottom Ash." Geoconfine 93 Edited by Arnould, Barres and Come. Rotterdam, The Netherlands, pp 591. 1993

53 Kluge G., Saalfeld H. and Dannecker W. "Untersuchungen des Langzeitverhaltens von Mullverbrennungsschlacken beim Einsatz in Stra Benbau Forschungsbericht Nr. 10303006, Umweltforschungsplan des Bundesministers des Innnern, Berlin 1981

54 Lewis K., Bradshaw K., Blakey N.C., Turrel J., Henning S.M. and Flavin R.J. "Leaching Tests for Assessment of Contaminated Land. Interim NRA Guidance". National Rivers Authority. 1993

55 Bodenam F. Azaroual M. and Piantone P. "Forecasting the Long-Term Behaviour of MSWI-BA; Rapid Combined Tests. Waste Materials in Construction. Ed. Woolley, G.R., Goumans. J.J. J. M. and Wainwright, P.J. Elsevier Science 2000.

56 Koralewska R.and Faulstich M. "Process Integrated Carbonation of Bottom Ashes". Proceedings of International Symposium; Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

57 Westiner E. M.and Löcherer Th. Wörner. "Volume Stability of Hydraulic Bound MSWI Ash." Proceedings of International Symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

58 Wainwright P.J., J.R. Barton and Cresswell D.J.F. "The Long-Term Performance of Untreated Bottom Ash, and the Production and Use of a Lightweight Synthetic Aggregate from the Bottom Ash Fine Fraction." Proceedings of International Symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

59 Paine K.A., Dhir R. K.and Doran V.P.A. "Unprocessed and Processed Incinerator Ash as a Cement Bound Material."Proceedings of International Symposium: Use of Incinerator Ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

60 Frantz G.C. and Demars K.R. "Ash Reutilization Research at the University of Connecticut". Proceedings of International symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

61 Karpinski S., Zhang X., Gress D., Eighmy T. and Janoo V. "A Physical Evaluation of Municipal Solid Waste Grate Ash as an Aggregate Substitute in Alphatic Concrete." Proceedings of International symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

62 Czernin W. "Cement Chemistry and Physic for Civil Engineers". London, Grosby Lockwood. 1962

63 ENV 197-1.1992. Cement. Composition, Specifications and Conformity Criteria. Common cements

64 Yousuf M., Mollah A., Rajam K., Vempati T., Lin C. and David L.Coke. "The Interfacial Chemistry of Solidification/Stabilisation of Metal in Cement and Pozzolanic Material System". Waste Management, Vol.15 No.2 , pp 137-148. 1995

65 Lea's ."Chemistry of Cement of Cement and Concrete". Chapter 4: The Constituents and Specification of Portland Cements. Fourth edition. Ed by Peter C. Hewlett 1998

66 Lea's ."Chemistry of Cement of Cement and Concrete". Chapter 6: Hydration, Setting and Hardening of Portland Cements. Fourth edition. Ed by Peter C. Hewlett. 1998

67 Leach W. "The influence of gypsum on the hydration and properties of Portland cement pastes". Proceedings of the American Society for Testing Materials, Vol. 46. 1946

68 Haskell WE. "Three Factors Govern Optimum Gypsum Content". Rock Product 62, 108.1959

69 Ost B.W. "Optimum Sulfate Content of Portland Cement; Optimum Amount of Gypsum. Ceramic Bulletin 53, pp 579-82. 1974

70 Bentur A. "Effect of Gypsum on the Hydration and Strength of C_3S Pastes". Journal of ther American Society, No 59, pp 210-213. 1976

71 Jawed I. and Skalny J. "Alkalis in Cement". Cement and Concrete Research. Vol 8 pp 37-52. 1978

72 Diamond S. "Effect of Two Danish Fly Ashes on Alkali Contents of Pore Solutions of Cement -Fly Ash Pastes. Cement and Concrete Research Vol 11 pp383-94. 1981

73 Luke K. and Glasser F.P. "Time Temperature Dependent Changes in the Internal Constitution of Blended Cement. II Cement, Vol. 3 pp 179-91.1988

74 Taylor H.F.W. "A Method for Predicting Alkali ion Concentration in Cement Pore Solutions". Adv. Cement Research 1, pp 5-16. 1987

75 Sung-Yoon Hong and Glasser F.P. "Alkaline Binding in Cement Pastes. Part I. The C-S-H phase". Cement and Concrete Research 29 pp 1893-1903. 1999

76 Lea's ."Chemistry of Cement of Cement and Concrete". Chapter 8: Physiochemical and mechanical Properties of Portland Cements. Fourth edition. Ed by Peter C. Hewlett. 1998

77 Glasser F.P. "Properties of Cement Waste Composites". Waste Management Vol 16, Nos, 1-3 pp. 159-168. 1996

78 Neville. A. M. "Properties of Concrete". Chapter 2: Cementitious Materials of Different Types. Ed. Longman Group Limited, fourth and Final edition. 1995

79 Glasser F. P. "Fundamental Aspects of Cement Solidification and Stabilisation". Journal of Hazardous Materials 52, pp 151-170. 1997

80 Diamond S. and Lopez-Flores F. "Comparative Studies of the Effects of Lignitic and Bituminous Fly Ashes in Hydrated Cement Systems". Diamond Ed., Porc MRS Symp, Mat Res Society, Pittsburg, PA pp 112-123. 1981

81 Beunfeld N.R. and Ahmed Y.H. "GGBS-Based S/S of Toxic Waste". A study undertaken for Appleby Group. Deparment of Civil Engineering Imperial College .1992

82 Park C.K. "Hydration and Solidification of Hazardous Wastes Containing Heavy Metals Using Modified Cementitious Materials". Cement and Concrete Research Vol. 30 pp 429-435. 2000

83 Li X.D., Poon C.S., Sun H, Lo I.M.C. and Kirk D.W. "Heavy Metal Speciation and Leaching Behaviour in Cement Based Solidified /Stabilised Waste Materials". Journal of Hazardous Materials A82 pp215-230.2001

84 Taylor, H.F.W. "Cement Chemistry". Chapter 12: Concrete Chemistry. 2nd Ed. Published by Thomas Telford. 1997

85 Duchesne J. and Bérubé M.A. "Long-term Effectiveness of Supplementary Cementing Materials Against Alkali-Silica reaction". Cement and Concrete Research, Vol. 31 pp 1057-1063. 2000

86 Medhat H. Shehata, Michel D.A. Thomas and Roland F. Bleszynski. "The Effects of Fly Ash Composition on the Chemistry of Pore Solution in Hydrated Cement Paste". Cement and Concrete Research, Vol 29, pp. 1915-1920. 1999

87 Medhat H. Shehata and Michel D.A. Thomas. "The Effect of Fly Ash Composition on the Expansion of Concrete Due to Alkali-Silica Reaction". Cement and Concrete Research, Vol 30, pp. 1063-1072. 2000

88 Gisli Gudmundson and Hakon Olafsson. "Alkali-Silica Reaction and Silica Fume 20 Years of Experience in Iceland". Cement and Concrete Research, Vol. 29, pp. 1289-1297. 1999

89 Hills C.D., Sollars C.J. and Perry R. "A Calorimetric and Micro-Structural Study of Solidified Toxic Wastes. Part 1: A Classification of Cement/Waste Interference Effects. Waste Management, 14(7) pp 589-599. 1994

90 Hills C.D., Sollars C.J. and Perry R. "A Calorimetric and Micro-Structural Study of Solidified Toxic Wastes. Part 2: A Model for Poisoning of Cement Hydration. Waste Management, Vol. 14(7) pp 601-612. 1994

91 Cocke D.L. and Mollah M.Y.A. "The Chemistry and Leaching Mechanisms of Hazardous Substances in Cementitious Solidification/Stabilisation Systems." ACS Series Book on

Chemistry and Micro-structure of Solidified Waste Forms. Roger D. Spence (ed) pp 187-242. Lewis Publishers, Boca Raton, Fl.1993

92 Cocke, D.L. "The Binding Chemistry and Leaching Mechanisms of Hazardous Substances in Cementitious Solidification/Stabilisation Systems." Journal Hazardous Materials Vol. 24 pp 231-253. 1990

93 Glasser F.P. "Chemistry and Microstructure of Solidified Waste Forms". R.D. Spence (Ed). Lewis Publishers, Boca Raton, FL, pp 1. 1993

94 Vandecasteele C., Dutré V., Geysen D. and Wauters G. "Solidification/Stabilisation of Arsenic Bearing Fly Ash from the Metallurgical Industry. Immobilisation Mechanism of Arsenic". Waste Management, Vol. 22, pp 143-146. 2002

95 Roy A and Cartledge F.K. "Long-term Behaviour of a Portland Cement-Electroplating Sludge Waste Form in Presence of Copper Nitrate". Journal of Hazardous Materials, Vol. 52 pp 265. 1997

96 Park J.Y. and Batchelor B. "Prediction of Chemical Specification in Stabilized/Solidified Wastes Using a General Chemical Equilibrium Model II: Doped Waste Contaminants in Cement Pore Waters". Cement and Concrete Research, Vol. 29 pp 99-105. 1999

97 Trussell S. and Batchelor B. "Chemical Characterisation of Pore Water of Solidified Hazardous Waste". Stabilisation and Solidification of Hazardous, Radioactive and Mixed Wastes: 3rd ASTM STP 1240. 1996

98 Wang S. and Vipulannadan C. "Solidification/Stabilisation of Cr(VI) with Cement. Leachability and XRD Analyses". Cement and Concrete Research, Vol. 30, pp 385-389. 2000

99 Van Eijk R.J. and Brouwers H.J.H. "Modelling the Effect of Waste Components on Cement Hydration." Waste Management 21 pp 279-284. 2001

100 Asavapisit S., Fowler G. and Cheeseman C.R. "Solution Chemistry During Cement Hydration in the Presence of Metal Hydroxide Wastes". Cement and Concrete Research, Vol. 27, No. 8, pp 1249-1260. 1997.

101 Conner J.R. and Hoeffner S.L. "A Critical Review of Stabilisation/Solidification Technology". Critical Reviews in Environmental Science and Technology, Vol. 28 Issue 4 pp 397-462. 1998

102 Stumm W. and Moragan J.J. "Aquatic Chemistry". 2nd Ed. John Wley. 1981

103 Neville A.M. Properties of Concrete. Chapter 10: Durability of Concrete. Fourth and Final Edition. 1995

104 Neville A.M. Properties of Concrete. Chapter 11: Effects of Freezing and Thawing and of Chlorides. Fourth and Final Edition. 1995

105 Auer S., Kuzel H.J., Pollmann H. and Sorrentino F. "Investigation of MSW Fly Ash Treatment by Reactive Calcium Aluminates and Phases Formed". Cement and Concrete Research, Vol. 25 Nos. 6, pp 1347-1359. 1995

106 Alba N., Vazquez E. Gasso S. and Baldasano J.M. "Stabilisation/solidification of MSW incineration residues from facilities with different air pollution control systems. Durability of matrices versus carbonation". Waste Management, Vol. 21, pp 313-323. 2001

107 Dumitru G., Vazquez T., Puertas F. and Blanco-Vareja M.R. " Influence of $BaCO_3$ on the Hydration of C_3A". Proceedings of the 10^{th} International Congress on Chemistry of Cement, Vol. 3, 3iii015. Ed by Dr. Harald Justnes. Goteborg 1997

108 Lea's ."Chemistry of Cement of Cement and Concrete". Chapter 10: Pozzolana and Pozzolanic Cements. Fourth edition. Ed by Peter C. Hewlett. 1998

109 Marsh B.K. and Day R.L. "Pozzolanic and Cementitious Reaction of Fly Ash in Blended Cements". Cement and Concrete Research, Vol. 18 pp 301-310.1988

110 Baoju L., Youjun W., Shiqiong Z. and Quanlian Y. " Influence of Ultra-Fine Fly Ash Composite on the Fluidity and Compressive Strength of Concrete". Cement and Concrete Research, Vol 30, pp 1489-1493. 2000

111 Goplan M.P. and Haque M.N. "Effect of Curing Regime on the Properties of Fly-Ash Concrete". ACI Materials Journal pp 14-19. 1987

112 Ramezanianpour A.A. and Malhotra V.M. " Effect of Curing on the Compressive Strength, Resistance to Chloride-Ion Penetration and Porosity of Concretes Incorporating Slag, Fly Ash or Silica Fume. Cement and Concrete Composites 17, pp 125-133.1995

113 Concrete Society. " The use of GGBS and PFA in Concrete". Technical Report No. 40. 1991

114 Pera P. Coutaz L. Ambroise J. and Chababbet M. "Use of Incinerator Bottom Ash in Concrete". Cement and Concrete Research, Vol. 27 No pp 1-5. 1997

115 Chang N.B, Wang H.P., Huang W.L. and Lin K.S. "The assessment of Reuse Potential for Municipal Solid waste and Refused-Derived Fuel Incineration Ash". Resources, Conservation and Recycling, Vol. 25 pp 225-270. 1999

116 Wainwright P.J. and Cresswell D.J.F. "Synthetic Aggregates form Combustion Ashes Using an Innovative Rotary Kiln". Waste Management, Vol. 21, pp 241-246. 2001

117 Filipponi P, Polettini R, Pomi R and Sirini P. "Physical and mechanical Properties of Cement-based Products Containing Incineration Bottom Ash". Waste Management. *Article in press.* 2002

118 Neville A.M. Properties of Concrete. Chapter 9: Elasticity, Shrinkage and Creep. Fourth and Final Edition. 1995

119 Odman S.T.A. "Effects of Variation in Volume, Surface Area Exposed to Drying, and Composition of Concrete on Shrinkage". RILEM/CEMBUREAU International Colloquium on Shrinkage of Hydraulic Concretes, Vol. 1, pp 20. 1986

120 Shoya M. "Drying Shrinkage and Moisture Loss of Super Plastizer Admixed Concrete of low Water Cement Ratio". Transactions of the Japan Concrete Institute, II-5, pp 103. 1979

121 Toxell G.E., Raphel J.M. and Davis R.E. "Long-time Creep and Shrinkage Tests of Plain and Reinforced Concrete". Proc. ASTM, 58 pp1101-20. 1958.

122 Hogan F.J. and Meusel. "Evaluation for Durability and Strength Development of a Ground Granulated Blastfurnace Slag". Cement, Concrete and Aggregates. CCAGDP, Vol. 3 No. 1, pp 40-52.1981

123 Khatri R.P. Sirivivatnanon V. and Gross W. "Effect of Different Supplementary Cementitious Materials on Mechanical Properties of High Performance Concrete". Cement and Concrete Research, Vol. 25, No. 1, pp 209-220. 1995

124 Wainwright P.J. "Concrete Technology and Design". Volume 3: Cement Replacement Materials. Chapter 4: Properties of Fresh and Hardened Concrete Incorporating Slag Cements. Ed Swamy RN .1986.

125 Odler I. and Röβler M. "Investigation on the Relationship Between Porosity, Structure and Strength of Hydrated Portland Cement Paste (II) Effect of Pore Structure and of Degree of Hydration". Cement and Concrete Research, 15, pp. 401-410, 1985

126 Röβler M. and Odler I. " Investigation on the Relationship Between Porosity, Structure and Strength of Hydrated Portland Cement Paste (I) Effect of Porosity". Cement and Concrete Research, 15, pp. 320-330, 1985

127 Takahashi T., Yamamoto K., Loku K., and Goto S. "Relationship Between Compressive Strength and Pore Structure of Hardened Cement Pastes". Advances in Concrete Research, 9, 33, pp. 25-30, 1997

128 Mallidi S.R. "Application of Mercury Intrusion Porosimetry on Clay Bricks to Assess Freeze-Thaw Durability". A Bibliography with Abstracts, Construction and Building Materials, 10, 6, pp.461-465, 1996

129 Lang E. and Geiseler J. "Utilisation of High Slag Blastfurnace Cement for High-Performance Concrete. Influence of Pore Structure and Permeability". Proceedings of the 10th International Congress on the Chemistry of Cement, Vol.4, Performance and Durability of Cementitious Materials, 4iv001, 4pp. Gothenburg, Sweden. 1997

130 Aldea C.M., Young F., Wang K. and Shah, S.P. "Effects Of Curing Conditions On Properties of Concrete Using Slag Replacement". Cement and Concrete Research, Vol. 30, pp.465-472. 2000

131 O'Farrell M., Wild S. and Sabir B.B. "Pore Size Distribution and Compressive Strength of Waste Clay Brick Mortar". Cement & Concrete Composites, Vol. 23 pp 81-91. 2001

132 Neville A.M. Properties of Concrete. Chapter 6: Strength of Concrete. Fourth and Final Edition. 1995

133 Feldman R.F. "The Effect of Sand/Cement Ratio and Silica Fume on the Microstructure of Mortars". Cement and Concrete Research. Vol. 16,pp 31-39.1986

134 Winslow D. and Ding L.. "The Pore Structure of Paste in Concrete". Cement and Concrete Research, Vol. 20 No. 2 pp 227-84. 1990

135 Fagerlund G. "Strength and Porosity of Concrete". Proceedings of the International Symposium, RILEM/IUPAC on Pore Structure and Properties of Materials, Part 2, Prague, pp. D51-D73. 1973

136 Fagerlund G. "The Elastic Moduli of Concrete". Proceedings of the International Symposium, RILEM/IUPAC on Pore Structure and Properties of Materials, Part 2, Prague, pp. D129-D141, 1973

137 Guerrero A., Goñi S., Macías A. and Luxán M.P. "Mechanical Properties, Pore Size Distribution, and Pore Solution of Fly Ash-Belite Cement Mortars". Cement and Concrete Research, Vol. 29, pp.1753-1758. 1999

138 Shi C. "Strength, Pore Structure and Permeability of Alkali-Activated Slag Mortars". Cement and Concrete Research, Vol.26, no.12, pp.1789-1799, 1996

139 Kolias S. "Investigation of the Possibility of Estimating Concrete Strength by Porosity Measurements". Materials and Structures, Vol. 27, pp.265-272, 1994

140 Watson K.L. "A Simple Relationship Between the Compressive Strength and Porosity of Hydrated Portland Cement" Cement and Concrete Research, Vol.11, pp.473-476, 1981

141 Pandey S.P. and Sharma R.L. "The Influence of Mineral Additives of the Strength and Porosity of OPC Mortar". Cement and Concrete Research, Vol. 30, pp.19-23, 2000

142 Mehta P.K. "Hardened Cement Paste; Microstructure and its Relationship to Properties". 8th International Congress on the Chemistry of Cement, Rio de Janeiro, pp.113-121, 22-27. 1986

143 Neville A.M. Properties of Concrete. Chapter 10: Durability of Concrete. Fourth and Final Edition. 1995

144 Hughes D.C. "Sulfate Resistance of OPC, OPC/fly Ash and SRPC Pastes: Pore Structure and Permeability". Cement and Concrete Research, Vol.15, pp.1003-1012, 1985

145 Guerrero A., Goñi S. and Macías A. "Durability of New Fly Ash-Belite Cement Mortars in Sulfated and Chloride Medium". Cement and Concrete Research, Vol. 30, pp.1231-1238. 2000

146 Young J.F. "A Review of the Pore Structure of Cement Paste and Concrete and its Influence on Permeability". ACI Publication, SP108-1, pp.1-18.

147 Santhanam M. Cohen M.D. and Olek J. "Mechanism of Sulfate attack: A fresh look Part 1: Summary of Experimental Results. Cement and Concrete Research Vol. 32 pp 915-921. 2002

148 O'Farrell M., Wild S. and Sabir B.B. "Resistance to Chemical Attack of Ground Brick -PC Mortar. Part:. Sodium Sulfate Solution". Cement and Concrete Research. Vol. 29 pp 1781-1790. 1999

149 Santhanam M., Cohen M.D. and Olek J. "Effect of Gypsum Formation on the Performance of Cement Mortars during External Sulfate Attack". Cement and Concrete Research, Vol. 33, pp. 325-332. 2003

150 Barker A.P. and Hobbs D.W. "Performance of Portland Limestone Cements in Mortar Prisms Immersed in Sulfate Solutions At 5ºC". Cement and Concrete Composites, Vol. 1 pp129-137. 1999

151 Larbi L.A. "Microstructure of the Interfacial Zone around Aggregates Particles in Concrete". Heron, 38 No. 1, 69 pp. 1993

152 Santhanam M., Cohen M.D. and Olek J. "Sulfate Attack Research - Whither Now? Cement and Concrete Research, Vol. 31, pp.845-851, 2001

153 Irassar E.F., Gonzalez M. and Rahhal. "Sulfate Resistance of Type V Cements with Limestone Filler and Natural Pozzolana". Cement and Concrete Composites, Vol. 22 pp 361-368. 2000

154 Osborne G.J. "Durability of Portland Blast-Furnace Slag Cement Concrete". Cement and Concrete Composites. Vol. 21, pp 11-21. 1999

155 De Groot G.J., Hohberg I., Lamers F.J.M. Van der Veen A.M.H., Wassing, Quevauviller Ph. "Development of Leaching Method for the Determination of the Environmental quality of Concrete". European Commission BCR Information 1997

156 Sanchez F., Barna R., Garrabrants A. Kosson D.S and Moszkowicz P. "Environmental Assessment of a Cement-Based Solidified Soil Contaminated with Lead". Chemical Engineering Science, Vol. 55 pp 113-128. 2000

157 Quenee B., Li G., Siwak J.M. and Basuyau V. "The Use of MSWI Bottom Ash as Aggregates in Hydraulic Concrete". Waste Materials in construction. Woolley G.R., Goumans J.J.J.M. and Wainwright P.J. Elsevier Science. 2000

158 Polettini A., Polettini S., Pomi R. and Sirini P. "Physical Properties and Acid Neutralisation Capacity of Incinerator Bottom Ash-Portland Cement Mixtures". Waste Materials in Construction. Woolley G.R., Goumans J.J.J.M. and Wainwright P.J. Elsevier Science. 2000

CHAPTER 3: MATERIALS, TECHNIQUES AND TEST METHODS

3.1 SCOPE

This chapter includes three main sections; the first section consists of a summary of materials and instruments employed. The second section describes the techniques and the measuring procedures. The techniques include those used to determine the concentrations of metals, sulfates and chlorides in leachates (Chapters 5 & 8) and to examine the porosity of mortar (Chapters 6). The third section includes the collection method and general procedures used throughout the experimental chapters. General procedures include reduction of samples, preparation of mortar, and data analysis strategy.

3.2 MATERIALS

3.2.1 Reagents

- Water

Deionised water with a specific conductivity not higher than 0.2mS/m at 25°C was used to carry out the chemical analysis and leaching procedures.

- Buffer solutions

The following three buffer solutions were used for calibration of pH-meter:

a) phthalate: pH=4 at 20°C

b) phosphate: pH=7 at 20°C

c) borate: pH=10 at 20°C

- Nitric acid

HNO_3 Aristar grade (purity 69%) was used for preparing 1% and 5% (v/v) nitric solutions. In addition, pure HNO_3 Aristar was required to acidify samples that had passed a leaching procedure.

- Solutions for sulfate resistance test

Two sulfate solutions were used to evaluate the sulfate resistance of mortar containing MSWI-BA. These were:

a) 5% sodium sulfate solution. This was prepared from Na_2SO_4 anhydride diluted with water (50 grams of Na_2SO_4 anhydride per kg of solution).

b) 5% magnesium sulfate solution. This was prepared from $MgSO_4.7H_2O$ diluted with water (102.36 grams of $MgSO_4.7H_2O$ per kg of solution).

- Standard solutions for Inductively Couple Plasma-Mass Spectrometry (ICP-MS) and Inductively Couple Plasma-Mass Spectrometry-Optical Emission Spectrometry (ICP-OES).

All calibration standard solutions prepared for the determination of metal concentrations, employing ICP-MS and ICP-OES techniques, were prepared from BDH Aristar solutions with concentration of 1000 mgL^{-1}. To obtain the desired range of concentrations, several dilutions with 1% HNO_3 were required. All standard solutions within a specific range of concentration were prepared from the same original solution. Thus, for ICP-MS and ICP-AES analysis, the standard solutions were prepared from a solution of $1mgL^{-1}$ and $100mgL^{-1}$ concentration respectively. Standard solutions were prepared monthly and stored in a fridge (temperature<10°C) during that time.

- Standards solution for ion chromatography

The standard solutions used for the determination of sulfates were prepared from sodium sulfate anhydrous granular 99.5% (Analar) and diluted with ultra pure water (Milli-Q RG) to achieve a solution with concentration of $100mgL^{-1}$. Standard solutions of 1, 2, 5 and $10mgL^{-1}$ were prepared from the original solution of $100mgL^{-1}$ and deionised water.

The standard solutions used for the determination of chlorides were prepared from sodium chloride 99.9% (Analar). The preparation of standard solutions was exactly the same as those mentioned above for sulfate standard solutions.

- Ion chromatography mobile phase and suppresser solution

a) The mobile phase (Sodium Carbonate & Sodium Hydrogen Carbonate) was prepared by dissolving 0.570 grams of $HNaCO_3$ and 0.784 grams of Na_2CO_3 with ultra pure water (Milli-Q RG) and diluted to 4L

b) The suppresser solution, Sulphuric Acid, was prepared by diluting 2.8ml of concentrated H_2SO_4 in 4L of ultra pure water.

3.2.2 Construction Materials

- Cement

The type of cement used in the main part of the experimental programme was Portland Cement 42.5N, identified as C-1. To ensure homogeneity of the cement used for all procedures, it was stored in airtight containers at 20±1°C and 65±5% RH. For comparative reasons, high C_3A cement was also used for one series of the sulfate resistance examination and was identified as C-2. Both cements conformed to BS 12:1996 (**1**). Table 3.1 shows the mineralogical compositions of both cements as provided by the manufacturer (Castle Cement).

Table 3.1 Mineralogical Composition of Cements

Cement Compound (% weight)		Portland Cement C-1	High C_3A Cement C-2
Tricalcium Silicate	(C_3S)	55.7	50.7
Dicalcium Silicate	(C_2S)	17.8	19.95
Tricalcium Aluminate	(C_3A)	7.1	11.17
Tetracalcium Aluminoferrite	(C_4AF)	8.5	6.80

- Aggregates

The aggregates included a class M sand that conformed to BS 882: 1992 (**2**) and a silica sand (SiO_2 content of approximately 70%). Class M sand and silica sand possess grains with diameters below 2.36mm. The aggregates were dried at 100°C for 24 hours before using. In order to avoid the presence of moisture, the aggregates were stored in sealed containers at 20±1°C and 65±5% RH.

Detailed physical and chemical characteristics of cement and aggregates used throughout the experimental programme are provided in Chapter 4 together with the physical and chemical examination of the fractions of MSWI-BA used as partial replacement of cement and sand.

3.3 INSTRUMENTS

- Compressive Strength Equipment

Compressive strength testing was performed in accordance to BS 1881 Part-116 (**3**). An Avery-Denison 7226/D/T 85248 machine with a loading rate of 45kN/min was used

for compressive strength testing. A special cube support (50mm x 50mm) was fitted to ensure consistency during testing. Compressive strength was calculated as follows:

$$C_s = \frac{F_A}{A} \qquad \textbf{Equation 3.1}$$

C_S = Compressive strength (N/mm²)

F_A = Maximum applied force (N)

A = Area of sample (mm²)

In addition, relative strength was calculated using Equation 3.2

$$C_R = \frac{C_S}{C_{REF}} * 100 \qquad \textbf{Equation 3.2}$$

C_R= Relative strength at a specific age (%)

C_{REF} = Compressive strength of the reference mix at the same age (N/mm²)

- Flexural Strength Equipment

Flexural tests were carried out on prisms that were used previously for length change determination. The flexural strength was tested in accordance with BS EN 12390 (4) using an Avery-Denison 7226/D/T 85248 apparatus with a loading rate of 5 to 10 KN/min. Flexural strength was calculated using Equation 3.3:

$$f_{cf} = \frac{F * l}{d_1 * d_2^2} \qquad \textbf{Equation 3.3}$$

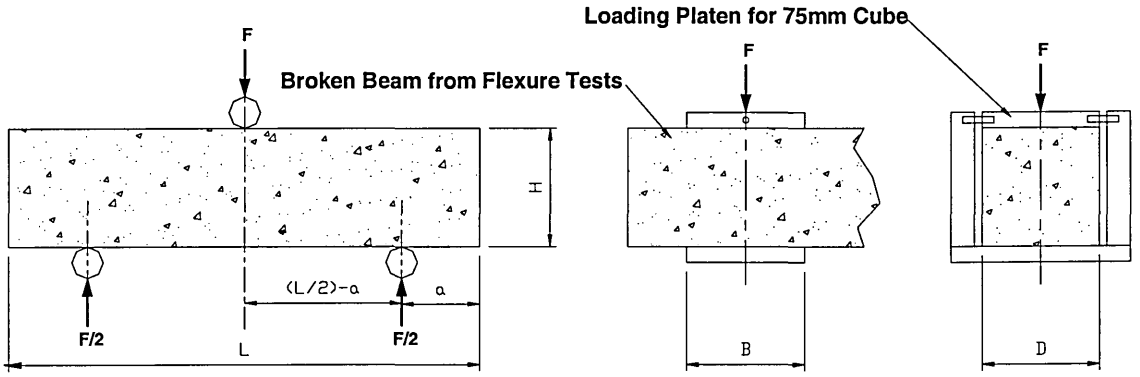
f_{cf}= flexural strength in N/mm^2

F= maximum load in N

l= distance between the supporting rollers in mm

d_1 and d_2= lateral dimensions of the specimen in mm

Figure 3.1-(a) shows the loading diagram how flexural strength was determined. Figure 3.1-(b) shows one piece of a broken beam after flexural testing and the loading diagram to determine compressive strength.



(a) Flexure Tests Loading Diagram

(b) Compressive Strength Loading Diagram - Confined Compression Test

Figure 3.1. (a) Loading diagram for flexural testing; (b) broken beam after flexural testing and loading diagram for compressive strength.

- Length Change

Length change was measured using two methods:

- Method A – Determination of change in length for prisms immersed in sulfate solutions (Chapter 7). Two inserts were cast into the end of prism of 40*40*160mm in size. The change in length between insets was measured using a dial gauge fixed to a steel frame (See Figure 3.2). The change in length, in percentage, at different exposure period was calculated using Equation 3.4:

$$\frac{\Delta L}{L_o} = \left(\frac{Rt - Ro}{lo}\right) * DG * 100 \qquad \textbf{Equation 3.4}$$

Where:

$\Delta L/L_0$= Change in length over the original length

R_t = New gauge reading after time 't'

R_o = Original gauge reading

lo = Original length of the prism,160mm

DG = Dial gauge factor (one division was equal to 1mm)

- Method B – Determination of change in length for prisms subjected to drying shrinkage (Chapter 6). Two demec-studs were attached on each face of prism of 75 x 75 x 300 in size at a spacing of 200mm (see Figure 3.2). The change in length between the studs was tested in accordance with BS 1881-206:1986 (**5**). A gauge was used to measure this length change. The change in length was expressed in terms of micro-strains (μ_s). The micro-strains were calculated using Equation 3.5

$$\mu_s = \frac{\Delta L}{L_0} = (R_o - R_t) * (GF) * 10^6 \qquad \textbf{Equation 3.5}$$

Where:

μ_s = micro-strains

$\Delta L/L_0$= Change in length over the original length

R_o = Original gauge reading

R_t = New gauge reading after time 't'

GF = Demec gauge factor (1.077×10^{-5})

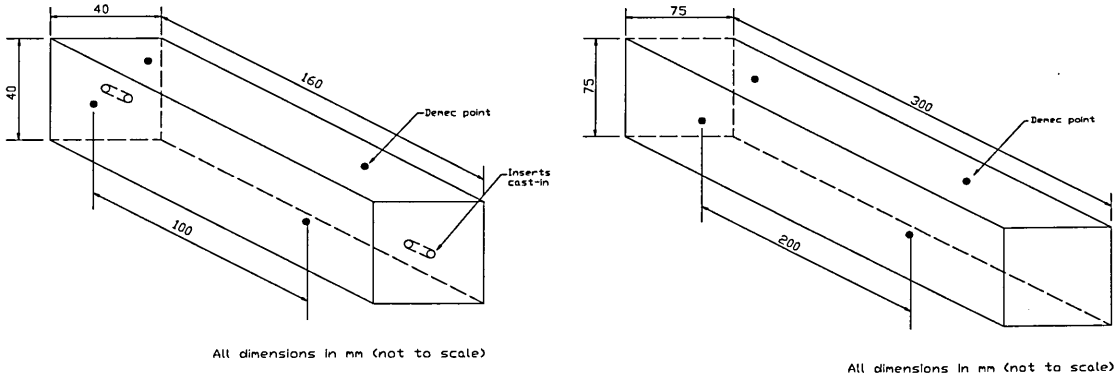


Figure 3.2. Insert cast and Demec to measure change in length in prism size of 40mm*40mm*160mm and 75mm*75mm*300mm and

- pH meter

An electrometric HI 931402 microprocessor pH-meter with an accuracy of ± 0.01 units at 25^0C was used to determine the pH of samples. The pH-meter has a temperature compensation facility and slope correction in milli-volts per pH value.

- ICP-OES Spectrometer

An Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used to determine the concentrations of elements (e.g. Ca, Na, K, Si, Fe, Al, Mg) in solution whose concentrations ranged from 1 to 1000 mgL^{-1}. Table 3.2 provides operational conditions of the ICP-OES (Spectro Instruments, Kleve, Germany). Further details about ICP-OES are given in section 3.4.1.1.

- ICP-MS

Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used to determine the concentrations of elements (e.g. Ni, Cr, Se, As, Mo, Hg) in solutions whose concentrations were below $1mgL^{-1}$. The operation conditions of the ICP-MS HP 4500 (Hewlett Packard, Yokogawa Corporation, Japan) are given in Table 3.3.

Table 3.2. ICP-OES Operational Conditions

Torch	Three piece torch
Spray chamber	Cyclonic
Nebuliser	Cross flow
Sample introduction	Peristaltic pump
Solution uptake rate	0.8 ml min^{-1}
Nebuliser gas flow rate	1.0 L min^{-1}
Nebuliser gas pressure	234 kPa
Measurement time	300 sec

Table 3.3. ICP-MS operation conditions

Torch	Fassel torch
Spray chamber	Cyclonic
Nebuliser	Babington
Sample introduction	Peristaltic pump
Solution uptake rate	0.8 ml min^{-1}
Nebuliser gas flow rate	1.28 L min^{-1}
Nebuliser gas pressure	590 kPa
Integration Time	3
Detector mode	Dual mode

- Chromatography apparatus

Sulfate and chloride concentrations in leachates were determined using a Dionex. Details of the Dionex QIC analyser are provided in Table 3.4.

Table 3.4. Dionex analyser operation conditions

Elements	**Types**
Column type	Dionex Ion-pac AS4A-SC 4mm (10-32)
Guard column	Dionex Ion-pac AG4A-SC 4mm (10-32)
Pump	Piston
Membrane	Anion Micro Membrane Suppressor Mod AMMS-I
Integrator	3395 Agilent

- X-ray Fluorescence Spectrometer

The determination of oxide contents for cement and MSWI-BA was carried out using an X-Ray fluorescence spectrometer, Philips 2400. Samples were fused at 1250°C for 12mins through a mixture of lithium tetraborate and lanthanum oxide, forming a glass bead that is suitable for X-ray fluorescence testing. The intensities of the fluorescent X-ray of the required elements are measured and the chemical composition of the samples is determined by reference to previously established calibrations. Results were reported as percentage of the oxide concentrations.

X-ray fluorescence spectrometry is considered an appropriate method to employ for the determination of major oxide contents of cement (**6**) except for sodium and elements whose atomic numbers are smaller than sodium. X-ray fluorescence spectrometry involves the following steps;

1. Radiation of samples by using a beam of X-ray or a radioactive source,
2. Excitation of the element in samples by absorption of the primary beam,
3. Emission of characteristics X-ray fluorescence by elements contained in samples,
4. Measurement of the emission and correlation with concentrations.

- Porosimeters

The examination of porosity and pore size distribution was conducted using two porosimeters, the Pascal 140 and 240. Both apparatus were supplied by CE Instruments. The porosimeters apply pressure to a sample confined in mercury and then records the intrusion pressure and the amount of mercury intruded into the sample. Both instruments are connected to an external PC for data analysis.

The Pascal 140 apparatus is used to prepare samples and to measure the porosity and pore size distribution of solids with pores between 1.9 and 300μm in diameter by applying a pressure from 0.1kPa to 100kPa. The Pascal 240 apparatus is used to measure the porosity of solids with pores 0.007 to 15μm in diameter by controlling the pressure generation between 0.1MPa to 200MPa.

3.4 TECHNIQUES

3.4.1 Inductively Coupled Plasma

Inductively Coupled Plasma (ICP) is one of the most important and widely used excitation sources used for atomic emission spectrometry. ICP allows rapid multi-

element determinations for different matrices at a wide range of concentrations. Atomic spectroscopy methods consist of the separation of sample constituents into free atoms or simple ions followed by the measure of absorption or emission of radiation produced as a result of the excitation of a part of atoms or ions of the samples. Atoms either emit or absorb discrete radiations as a function of type of atom examined (**7**). That fact is used to distinguish between different elements.

Plasma is an electrical conducting gaseous mixture, containing cations and electrons, whose net charge approaches zero. In argon plasma, Ar ions and electrons are the principle conducting species, although cations from samples are present in lesser amounts. Ar ions are capable of absorbing sufficient power from an external source, to maintain the temperature at which further ionisation sustains the plasma indefinitely.

A typical ICP source, known as a torch, consists of concentric quartz tubes through which argon flows (see Figure 3.3). Surrounding the top of the outer tube is an induction coil that is energised by the radio frequency generator creating a changing magnetic field. To initiate the ionisation of the flowing gas, a discharge from a Tesla coil or a pilot spark is applied to flowing argon. Ions and their associated electrons interact with the fluctuating magnetic field and then flow in a closed annular path within the coil. The resistance of ions and electrons to move produces heat. The temperature of the plasma formed in this way is high enough to require thermal isolation, which is achieved by flowing argon tangentially around walls. The tangential flow cools the inside walls of the centre tube and plasma.

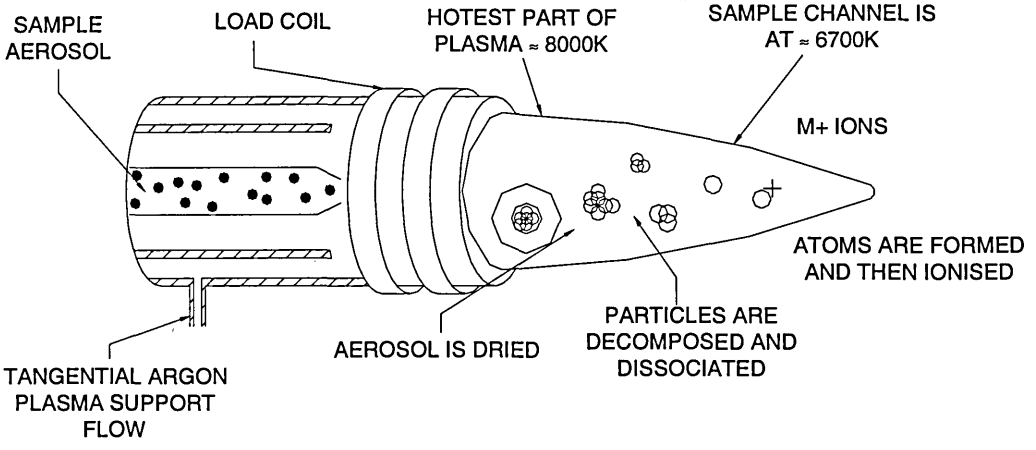


Figure 3.3 ICP Torch

An ICP is a high temperature excitation source providing a high degree of selectivity, good accuracy and precision. Based on these characteristic, ICP combined with optical emission spectrometry (OES) and mass spectrometry (MS) were employed to analyse concentrations above and below $1 mgL^{-1}$ respectively. Thus, in most of the literature

regarding leaching of bound and/or un-bound MSWI residues, ICP-OES technique has been used to determine the concentration of elements such as Ca, Na, K, Fe, Si, Zn, Cu (**8**, **9**, **10**) and ICP-MS has been employed for low concentrations of the same elements and other elements such as Pb, Cu, Cd, Cr (**9, 10**).

3.4.1.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The inductively coupled plasma combined with optical emission spectrometer (ICP-OES) includes a conventional ICP excitation source and an optical polychromator spectrometer. The ICP-OES employed allows concentrations from 1 to 100mgL^{-1} to be determined for a broad range of elements and different samples. ICP-OES technique is not affected significantly by inter-element interferences due to the ICP excitation source used. Figure 3.4 shows an ICP-OES with a polychromator. Samples are pumped into the nebuliser spray chamber where with argon gas form an aerosol of fine droplets.

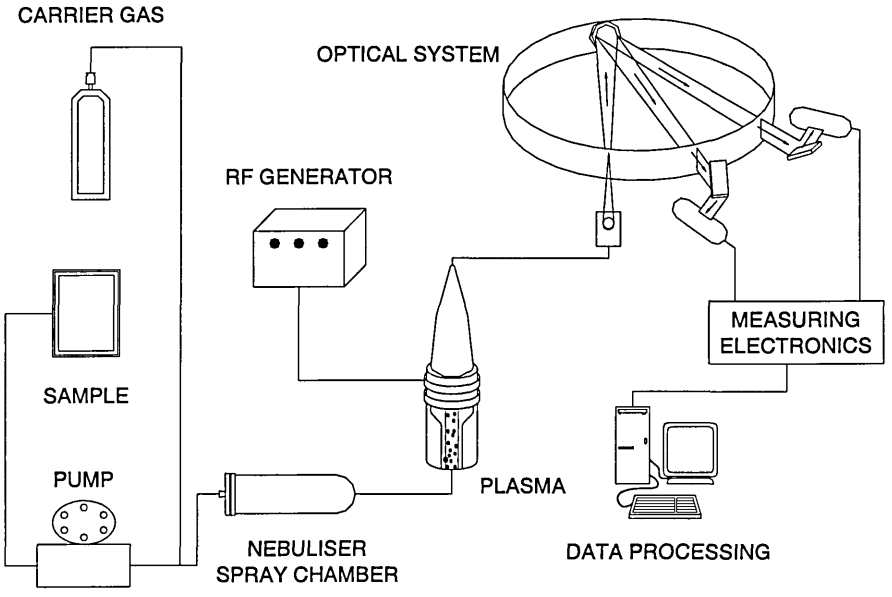


Figure 3.4. Schematic diagram of ICP-OES polychromator

The argon carries the finest droplets through the spry chamber and introduces them into the plasma where the sample is atomised and ionised as explained in section 3.4.1. The atoms and ions contained in the plasma vapour are raised to excited energy levels. These energy levels have a short lifetime and atoms drop back to the ground state, emitting a photon with energy equal to $h\nu$(h=constant and ν=wave frequency). The radiation emitted passes to an optic polychromator spectrometer. By definition, an optic emission spectrometer provides information about the intensity of radiation emitted as a function of wavelength or frequency (**11**). Polychromator spectrometers employ a series of photomultiplier tubes for detection of wavelengths for each element examined. Each element only emits several specific or discrete wavelengths that are

converted to an electrical signal in the transducer. The radiation intensity is proportional to the concentration of the element in the sample. Concentrations of each element examined are calculated internally by comparison with a previously stored set of calibration data.

3.4.1.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) combines an ICP with a quadrupole mass spectrometer (MS). The former provides a high temperature ion source and the latter provides a high sensitivity detector; therefore good accuracy and precision at low concentration levels can be achieved. Mass spectrometric analysis involves, apart from atomisation and formation of a fraction of ions, the separation of the ions on the basis of their atomic mass to charge ratio (m/z) and the measuring of the ion current of each type of element.

Figure 3.5 shows schematically an ICP-MS system (**12**). The introduction of the sample into the spray chamber and the plasma torch in ICP-MS involve the same techniques that were discussed in ICP and ICP-OES sections. Once ions have been formed in the plasma, they pass into a zone named the interface, which consists of two water-cooled orifices called sampling and skimmer cones. The sampling cone, with a central aperture of 1mm is located between plasma and skimmer cone. The skimmer cone is located coaxially behind the sampling cone. The pressure between the cones is maintained at 100Pa by a rotary vacuum pump and is reduced continuously from behind the skimmer cones to the analyser chamber (0.1Pa). This allows continued sampling of the bulk plasma. The gas coming into the first low pressure stage expands depending upon the aperture size and sampling-skimmer cones distance. The bulk of the gas is pumped away by the rotary vacuum pump and a small fraction passes through the final aperture into the quadrupole mass analyser. An omega lens system, which is located before the mass spectrometer, serves to focus the ions coming from the skimmer into the mass filter rejecting neutral atoms and minimising photons from ICP. The quadrupole consists of four parallel cylindrical rods that serve as electrodes. In the quadrupole, all the ions are converted to neutral molecules except those having a certain mass to charge ratio (m/z) that are allowed to pass through and reach the transducer or detector at any point in time. The detector measures the ion signal at each mass and stores it. Data is expressed as counts per second, which are directly proportional to the concentration of the element at that mass (**12**).

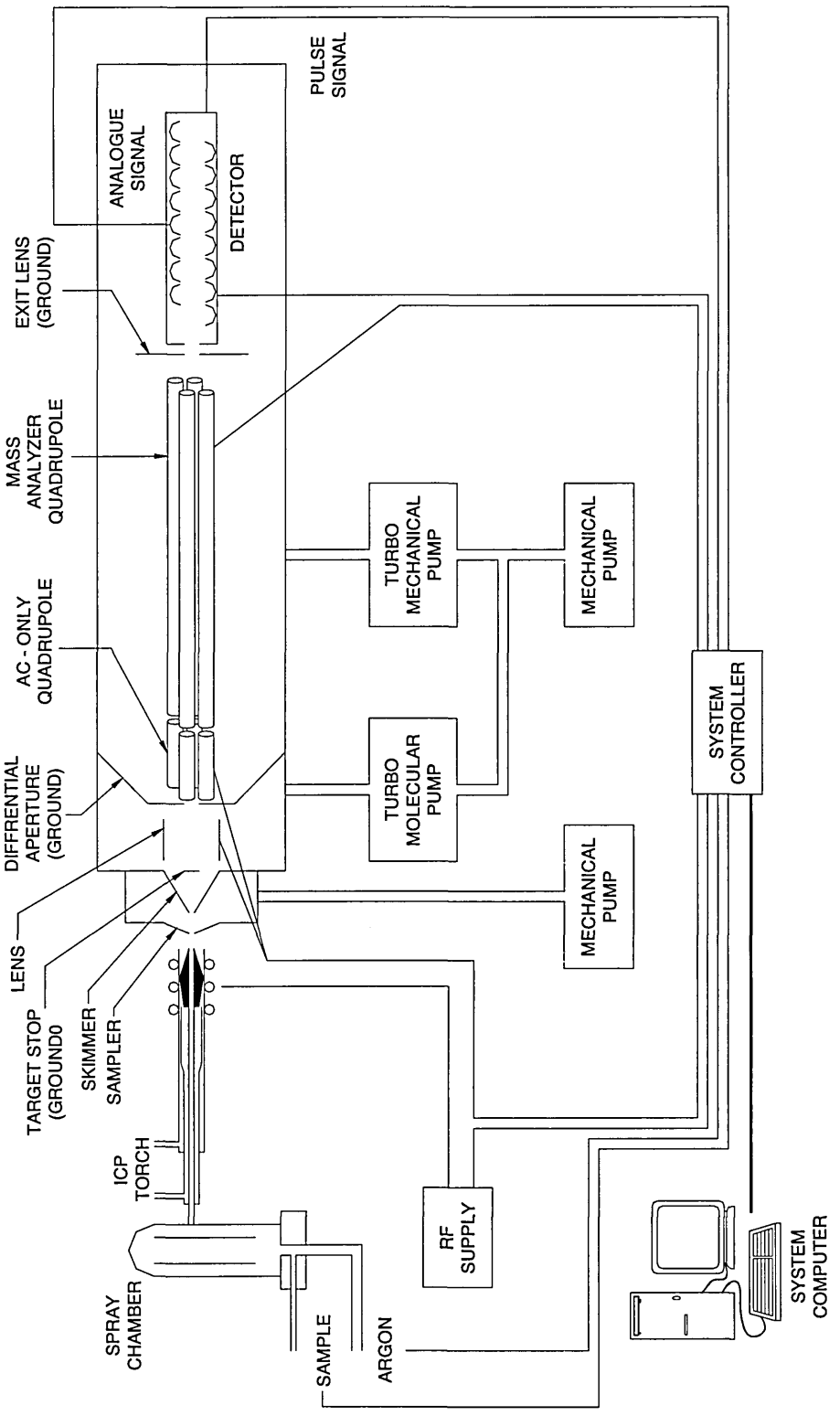


Figure 3.5 ICP-MS Diagram

Over the past decade there has been a significant increase in the use of ICP-MS for multi-element analysis because of its ability to accommodate solution samples easily (as in ICP-OES), its low detection limits and the possibility to carry out isotopic analysis (**13,14**). The disadvantages of ICP-MS compared with ICP-AES includes; a) higher instrument costs, b) instrument drift that can be as high as 5% to 10% per hour, and c) the occurrence of interferences which limit the application of ICP-MS.

Two types of interference may take place, mass spectroscopic and non spectroscopic interference. The former includes inter-element (e.g. ^{65}Zn and ^{65}Cu), poly-atomic (e.g. $^{80}Ar_2^+$ and ^{80}Se), and doubly-charged ion interferences (e.g. $^{88}Sr^{2+}$ and $^{44}Ca^{+2}$). The non-spectroscopic interferences are caused by the sample matrix that includes high suspension of solids, high mass elements, and easily ionised elements. Dilution of samples, election of an isotope free of interference, optimisation of the instrument, internal standardization, standard additions and matrix elimination (e.g. chromatography) are the common procedures to limit or inhibit the effects of spectroscopy and non-spectroscopic interferences (**12**).

3.4.1.3 Determination of Detection Limit for ICP-OES and ICP-MS.

In general, analytical instruments are designed to measure a wide range of signals and sample types. The response of the instrument is dependent upon the functional conditions and on the intrinsic nature of the samples tested. The detection limit is a measure of the analytical procedure. Detection limit is the minimum concentration or mass of analyte that can be detected at a known confidence level (**15**). Detection limit is dependent on the response of the blank and on the functional dependence of the analytical instrument on the concentration of analyte in sample. There are several methods to calculate the concentration in the limit of detection (**15**, **16**,**17**). Generally, the concentration in the limit of detection is equal to the concentration that gives a signal three times the standards deviation of the background signal. In addition, for quantitative analysis, it is recommended to work with concentrations that are ten times above the detection limit concentration (**17**) In this research programme, the concentration in detection limit was calculated using Equation 3.6.

$$\text{detection limit(concentration)} = 3S_b \qquad \textbf{Equation 3.6}$$

For each element analysed, the blanks used to determine the concentrations in limit of detection must follow the whole leaching procedure. Therefore, there was a need to determine the concentration in the limit of detection for each leaching series carried out. The number of replicated blanks depended on the leaching procedure conducted.

3.4.1.4 ICP-OES and ICP MS Procedures

- Samples Preparation

The leachates used for determination of metals were acidified to achieve a pH less than 2 to avoid further precipitations. Nevertheless, after 3 months, approximately 20% of leachates exhibited a white precipitate. For that reason, the determination of metals

was carried out as soon as possible and no longer than one month after leaching tests were conducted.

Contamination of leachates from glassware and filtration equipment was likely due to the fact that some of the elements analysed can commonly be found in the laboratory environment (e.g. Ca, Na, Zn, Cu and Pb). Thus, samples needed special care during storage and analysis to avoid contamination. Prior to utilisation, all materials in contact with samples were washed with a solution of nitric acid and de-ionised water several times. Despite the careful storage, contamination could not always be avoided and some samples had to be repeated several times.

- Selection of Wavelengths in ICP-OES

In order to examine possible inter-elemental interferences and identify the most appropriate wavelengths for each element, a wavelength scan was conducted. The wavelength scan was carried out using two solutions. The two solutions were prepared from BDH Aristar standards and they contained all elements that were subject to testing. The concentrations of the solutions were similar to the maximum and minimum expected concentrations for each element examined. Table 3.5 shows the wavelengths that were found more appropriate for the analysis of each element. The same wavelengths were used throughout all ICP-OES analysis of leachates either from unbound (Chapter 5) or bound MSWI-BA (Chapter 8).

Table 3.5 Wavelengths (nm) for ICP-OES

Si	251.61	**Ca**	317.933
Ba	455.40	**Na**	589.59
Ni	227.02	**K**	766.49
Pb	405.78	**Fe**	259.94
B	249.77	**Mg**	285.21
Cu	324.75	**Mn**	257.61
Zn	213.86	**Al**	308.21

- Optimisation of ICP-MS procedure

For leachates obtained from either unbound or bound BA, the elements subjected to ICP-MS analysis were B, Cr, Ni, Mn, Co, Cu, Zn, As, Se, Mo, Cd, Sn, Hg, Ba, and Pb. The concentrations of these elements ranged from μgL^{-1} for some elements to mgL^{-1} in others. In addition, each element can interact differently with those elements or compounds whose concentrations were high in the leachates. As a consequence of the

wide range of concentrations and different matrix interference in the leachates, the determination of concentrations using the ICP-MS technique required an optimisation for each element. Elements or compounds that are known as matrix or major elements/compounds possess high concentrations and can dominate solution properties.

Generally, maximum dilution of samples was used to reduce the matrix effects and contamination of ICP-MS spectrometer. In addition, internal standards, examination of most convenient isotopes and standard additions were also employed as methods to optimise ICP-MS analysis.

Internal standard (IS) is a useful way to compensate for sensitivity changes due to signal drift during the analysis. The appropriate IS elements must not be present in the samples solution and their atomic mass number and ionisation potential must be similar to that of the elements analysed. The IS concentration is recommended to be equal to or higher than the maximum concentration expected for the elements studied (**15**). For this research programme, scandium (Sc^{45}) was used as IS for the analysis of elements whose atomic masses were equal to or below Zn^{68}, whereas indium (In^{115}) was used for elements whose atomic masses were equal to or over Zn^{68}. Both internal standards were spiked in a constant amount to blanks, calibration standards and sample solutions.

Isotope examination was carried out to identify the isotope which did not show high degree of interference with the matrix. Appendix A provides the possible interference of major constituents of the matrix with the different isotopes of each element examined.

Table 3.6 shows the atomic mass of the isotopes examined for B, Cr, Ni, Cu, Zn, Se, Mo, Cd, Sn, Hg, Ba, Pb and Ba elements. For elements such as Mn, Co, and As, only one isotope was analysed because other isotopic forms are much less common.

Table 3.6: Isotopes used with ICP-MS

B	Cr	Ni	Cu	Zn	Se	Mo	Cd	Sn	Ba	Hg	Pb
10	52	58	63	64	78	96	111	117	137	200	207
11	53	60	65	66	80	97	112	118	138	201	208
				68	82	98	114	119		202	

Figure 3.6 shows the calibration curves for isotopes 52 and 53 of Chromium (Cr). Both isotopes exhibited low interference levels with matrix elements. They gave low background signal and good correlation coefficients (r). However, Cr^{52} gave higher

account ratios ("y" axes) than Cr^{53} because the former isotope is more sensitive than the latter Cr^{53}.

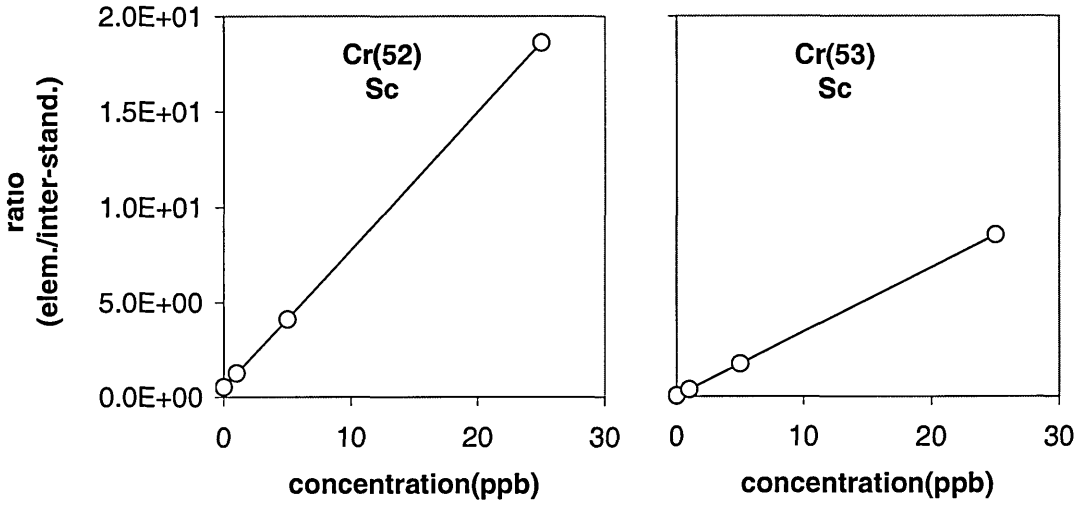


Figure 3.6. Isotopes 52 and 53 of Cr

Figure 3.7 shows the calibration curves for isotopes 78 and 82 of Selenium (Se). Isotope 78 gave higher level of interference with matrix element and/or argon ions than isotope 82. Isotopes 78 exhibited high background signal.

Isotopic assessment was only carried out for a specific number of samples because it was considered that those isotopes exhibiting much lesser interference were the same in the rest of the samples because of the similarity of the matrix.

The standard addition (SA) method is useful for determining ultra-trace samples and minimising the effects of the matrix on standards and samples. The SA method consists of spiking different known increments of standard solution of element analysed or analyte to sample aliquots of the same size. The calibration is made using the spiked samples and the un-spiked as blank. The concentration of sample analysed is calculated from the calibration curve. The curve of calibration obtained using SA can be converted to a calibration curve for analysing samples that possess similar matrix and concentrations.

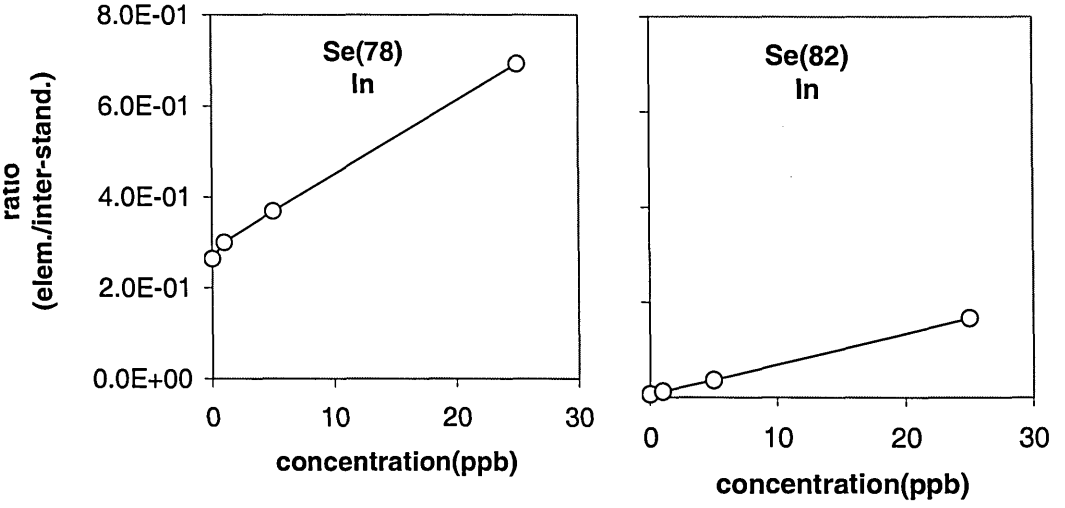


Figure 3.7. Isotopes 78 and 82 of Se

The optimisation of ICP-MS analysis is discussed in detail in Chapter 5, where the leaching behaviour of unbound BA is examined. The optimisation of ICP-MS analysis achieved in Chapter 5 was adopted to ICP-MS analysis for leached solutions of bound MSWI-BA in Chapter 8.

3.4.2 Chromatography

Chromatography is based on the separation of components of a mixture by passing the mixture through a column that retains some constituents longer than others. In all chromatographic separations the sample is transported in a mobile phase and then forced through an immiscible stationary phase. The two phases are chosen so that the components of the sample distribute themselves between the mobile and stationary phase to varying degrees. Those components that are strongly retained by the stationary phase move slowly with the flow of mobile phases while weakly retained constituents move rapidly. As a consequence of these differences in mobility, sample constituents are separated into discrete bands that can be analysed qualitatively and quantitatively.

Chromatographic methods are commonly categorised into different types based upon the nature of mobile and stationary phases (e.g. gas, liquid or supercritical phase) and the types of equilibria involved in the transfer of solutes between phases (**18**). For the analysis of sulfates and chlorides, ion chromatography seems to be the most common method (**8,9**).

3.4.2.1 Ion Chromatography

In ion chromatography, analytes (Cl^{1-} and SO_4^{2-}) are separated by an ion-exchange resin and detected by their electrical conductivity. Ion chromatography includes an ion-

exchange column and an eluent suppressor column. Since the conductivity of the eluent (mobile phases) is high enough to make it difficult to detect the conductivity change when analyte ions are eluted, the suppressor column is introduced to eliminate eluent before analytes are detected. Figure 3.8 shows a typical ion chromatographic separation of Cl^{1-} and SO_4^{2-} anions (**19**). Samples containing these anions are introduced into an anion exchange column or a separation column that is in carbonated form. Cl^{1-} and SO_4^{2-} anions form equilibria with the base resin and they are slowly displaced by the anions from mobile phases or eluent, CO_3^{2-}. The magnitude of the equilibrium constants, $Ke(Cl^{1-})$ and $Ke(SO_4^{2-})$ determine the affinity of the resin for one anion relative to the other. The resin retains longer the anion that possesses the higher equilibrium constant. In general, for strong base resin, the $Ke(SO_4^{2-})$ is higher than the $Ke(Cl^{1-})$, therefore the time of retention of SO_4^{2-} is higher than for Cl^{1-} anions (**20**). After a period of time, anions leave the separation column as NaCl and Na_2SO_4 and pass to the suppressor column. The suppressor column contains an acid resin loaded with H^+. In the suppressor column, Na^{+1} ions from the NaCl and the Na_2SO_4 are replaced by H^+, thereby forming H_2SO_4 and HCl. In order to regenerate the suppressor column after every run, a fibre membrane operating continuously is used. The eluent and the suppressor solution flow in opposite directions on either side of the permeable membrane. The regeneration of suppressor column is performed automatically by passing hydroxyl ions through the resin (**19,20**). Once eluent is separated from analyte ions, the conductivity of the examined ions can be measured. The analyser is then connected to an integrator that provides results of the integrated areas for each analyte.

Figure 3.8 shows ion-exchange and suppressor columns, the concentration versus time curves and the reactions that take place in each column.

3.4.2.2 Ion Chromatography Procedure

Sulfate and chloride concentrations were analysed in leachates of bound MSWI-BA in cement-based systems. The determination of both anions was not possible for leachates of unbound MSWI-BA samples. Leaching procedures conducted to examine the leaching behaviour of unbound MSWI-BA employed a high concentration of nitric acid. High concentrations of HNO_3 impeded to identity Cl^{1-} and SO_4^{-2} peaks in the chromatograms.

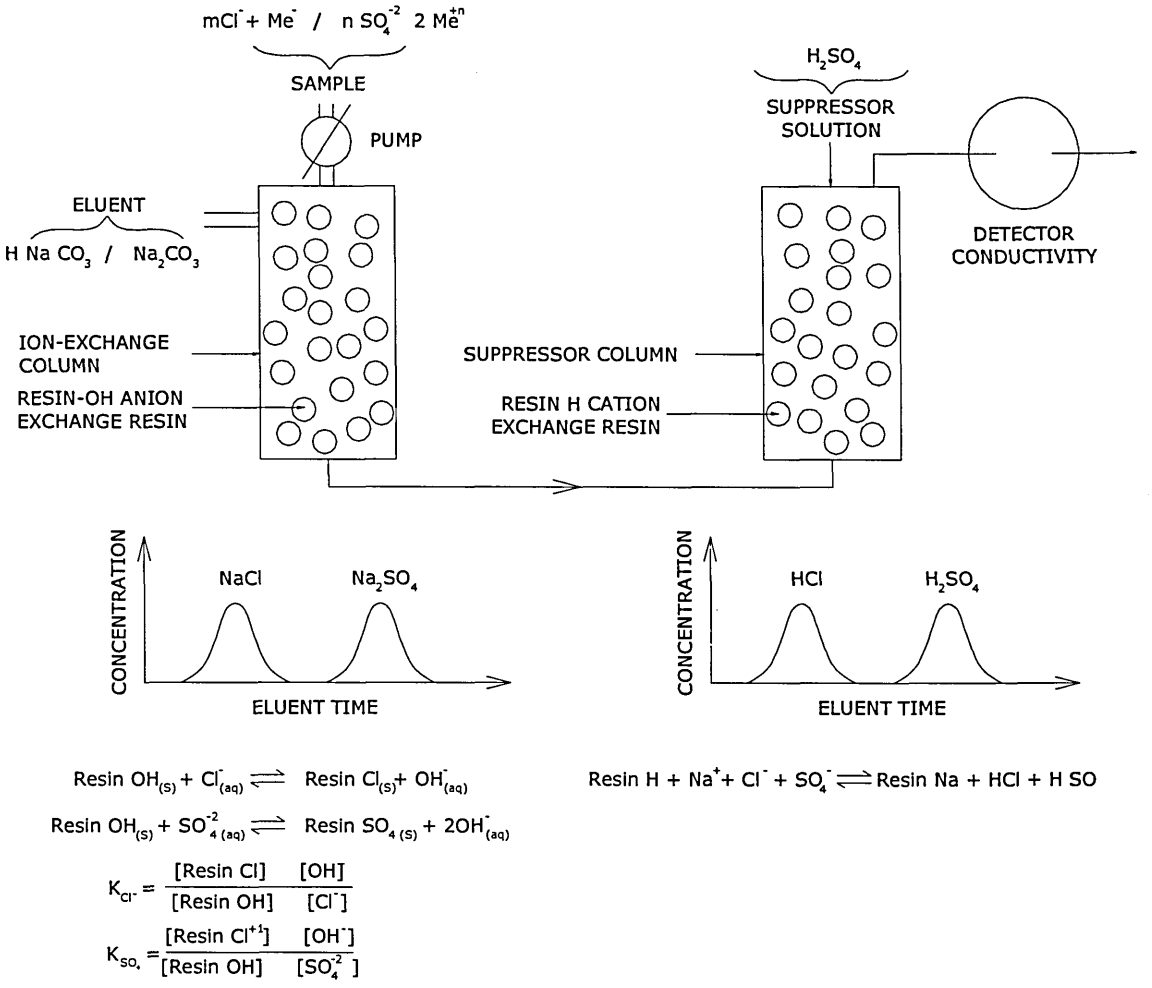


Figure 3.8. Schematic representation of Ion Chromatography

Leachates were analysed by injection of approximately 2ml of sample in the Dionex. Sulfate and chloride concentrations ranged from 5 to 20mgL^{1-} in leached samples. This range of concentration allowed the determination of the concentrations of both anions without diluting most of leachate sample. Dilution was only necessary in a few cases. The determination of sulfates and chlorides was conducted within a week of completion of leaching procedures.

Figure 3.9 shows the chromatograph for the standard solution containing 5mgL^{-1} of Cl^{1-} and SO_4^{2-}. The peaks for chlorides, nitrates and sulfates appeared at 2.723, 4.680 and 9.457 minutes respectively.

Figure 3.10 shows the chromatograph for a leachate of mortar specimen that contained MSWI-BA as partial replacement of cement and sand. MSWI-BA particle size used as replacement of cement had a diameter below 212μm. MSWI-BA particle size used as replacement of sand had a diameter that ranged between 212μm and 2.36mm. Leachant used consisted of de-ionised water acidified to reach a pH ranging between 2 and 4. Leachant was removed five times during the leaching procedure. The small

peak at 3.350 minutes correspond to an anion that was not subjected to examination whereas the peaks of chlorides, nitrates and sulfates are shown in the figure.

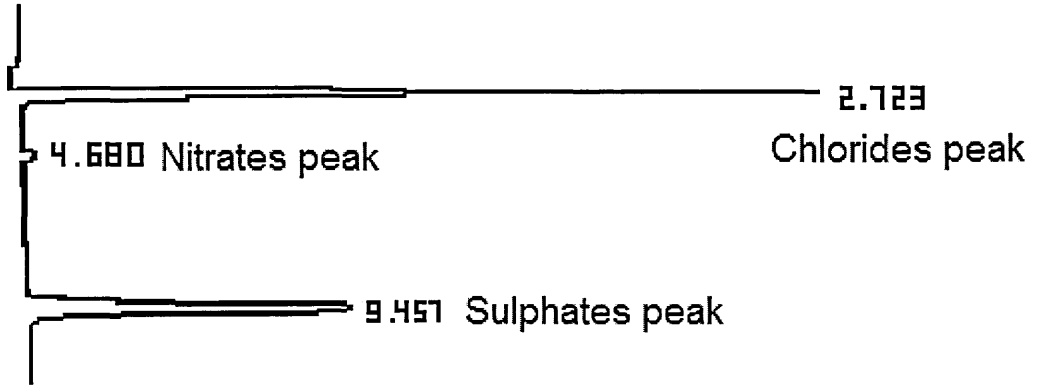


Figure 3.9. Chromatograph for a standard solution containing 5mgL^{-1} of Cl^{1-} and SO_4^{2-}

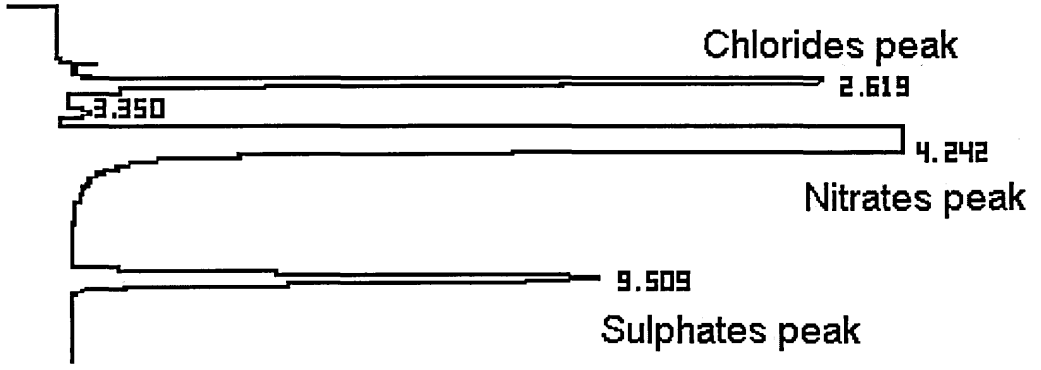


Figure 3.10 Chromatograph for a leachate of mortar sample containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively

The comparison of the chromatographs shown above (Figure 3.9 and Figure 3.10) indicates that despite the difference in matrices between standard solution and leachate solution of samples containing partial replacements of MSWI-BA, the retention times of Cl^{1-} and SO_4^{2-} were similar for the two types of solutions considered. The only noticeable difference between both chromatographs was the NO_3^{1-} peak. For the leachate sample, NO_3^{1-} peak was 78% of the total integrated chromatograph area whereas for the standard solution it was only 0.6% of the total integrated chromatograph area.

3.4.3 Mercury Intrusion Porosimetry

Mercury intrusion porosimetry (MIP) was used to determine the porosity and evaluate

pore diameters of mortar. The MIP technique is ideal for materials with medium to high porosities (**21**). The technique is based on the mercury's ability to act as a non-wetting liquid. Mercury penetrates into the pores of a sample under pressure and is not absorbed by the solid's pores because of its surface tension. MIP involves applying gradually an increasing pressure to a sample confined in mercury and results in mercury being intruded into the open pores of the sample. The pressure required to carry out the analysis depends on the size and structure of pores. The pressure applied is related to pore diameters as proposed by the Washburn equation (**22**). In the equation (Equation 3.7), the diameter of pores is directly proportional to surface tension of mercury, y, and the cosine of the contact angle, θ, and inversely proportional to the applied pressure, p :

$$d = \frac{-4y\cos\theta}{p} \qquad \textbf{Equation 3.7}$$

where:

p = absolute applied pressure

d = pore diameter

y = mercury surface tension

θ = contact angle between the liquid and the pore walls

Washburn's equation assumes the following:

a) All pores are cylindrical and equally accessible to the outer surface pores of the specimen,

b) No change in pore structure occurs during testing,

c) Mercury (Hg) surface tension and contact angle remain constant,

d) Intrusion pressure is in equilibrium.

It has been observed that contact angles depend on the nature of the samples examined (**23**). The values usually range from 125° to 152°, so an average value of 141.3° may be used. However, a value of 130° is generally used for cement pastes (**21,24**) and higher contact angles are used for mortar (**25,26**). In addition, it has been found that higher contact angles are required if paste or mortar materials contained waste as replacement of cement (**23**). The surface tension varies as a function of temperature. A range of 482.2 dynes/cm at 25°C to 472 dynes/cm at 50°C has been reported, and a value of 480dynes/cm is often used (**24,27**).

MIP is a widely used technique for determining the total pore volume and pore size distribution of cement-based materials (**22- 27**). However, this technique has several

limitations that lead especially to inaccurate pore size distribution interpretations (**21**,**24**,**28**). Some of these limitations are explained below:

a) The accessibility of mercury appears to be the most important concern to evaluate pore size distributions using this technique (**28**). Figure 3.11 shows the different structure of pores that can be found in porous materials, such as cement-based system specimens (**21**). Nearly all of the pores are in the interior of the specimen and these pores can be reached by the mercury through a percolate chain of intermediate pores of varying sizes and shapes. In a hypothetical pore system formed by a small open pore connected to a second large pore (See pore-C in Figure 3.11), the large pore does not require high pressure to be filled with Hg. However, this pore will not fill until the small pore reaches the high pressure required to fill its small diameter. This effect is known as ink-bottle and produces pore diameter distributions with an erroneously high average proportion of pore with low diameters and a small average proportion of pores with large diameters.

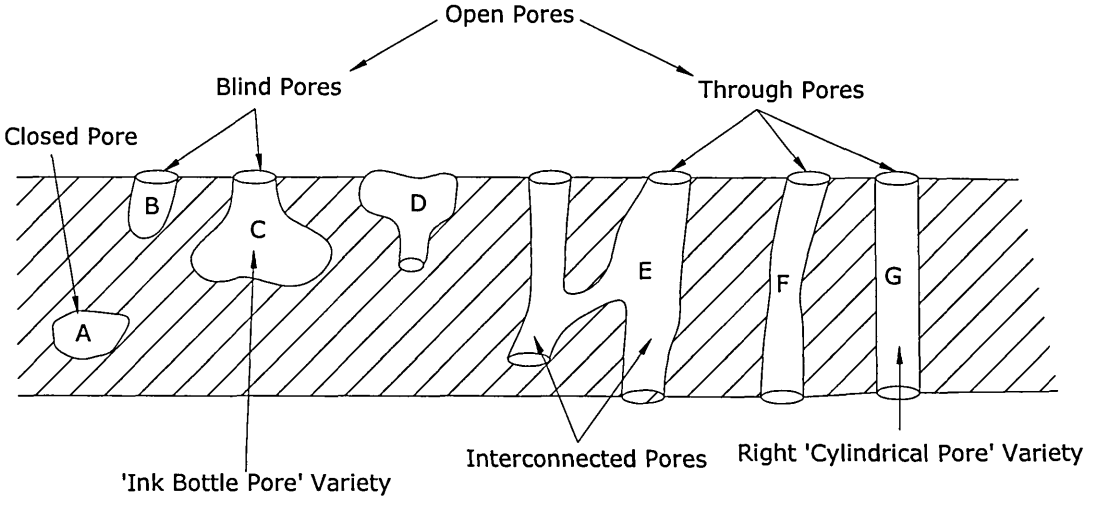


Figure 3.11. Types of pores that can be found in porous materials (21)

b) Another effect that can occur is pore blockage. Capillary pores can be blocked by gel pores and then solely connected to the gel pore net. The pore network is blocked by much finer connections at practically each step. Pore blockage effect will not affect the measurement of total porosity, so long as the pressure applied is high enough to breakdown the blockages and mercury is intruded into all of the open capillary pores. The effects of pore blockages should not affect the evaluation of the percentage of pores whose diameters are above 0.1μm.

c) The mercury may be unable to penetrate the narrowest pores, mainly gel pores, (**29**, **30**). Therefore, total porosity may be slightly lower than the actual value.

d) The contact angle is assumed constant throughout the analysis. However, it has been observed that contact angles vary as a function of age of cement paste and

binder compositions and also during the analysis (**23,31**). An error in the contact angle assumption that differs from the true value by 1° can result in an error of 2% in the determination of pore diameter when applying the Washburn equation (**32**).

e) The pressure used to force mercury into the pore network can damage the pore structure resulting in a false interpretation of the pore size distribution (**27,32**).

f) The Washburn equation model assumes that the system consists of cylindrical pores. But the investigation of Diamond (**28**) using Scanning Electronic Microscopy (SEM) analysis showed that pores were clearly not cylindrical.

Employing small samples and occurrence of micro-cracks facilitate the accessibility of pore. When micro-cracks occurs during fracture they can distort the true pore size distribution (**33**).

Different techniques (e.g. gas absorption, scanning electron microscopy) have been developed for measuring porosity and the characterisation of the pore size distribution of porous materials (**21**). The choice of the most appropriate method depends on the chemical and physical nature of the solid and the properties examined. For example the gas absorption technique is suitable for pores that lie in the micropore-mesopore region (e.g. with pore diameters between 0.0005μm and 0.05μm) whereas SEM is appropriate for the analysis of pores with large diameters (e.g. with pore diameters above 0.1μm).

3.4.3.1 MIP Procedure

- Samples Preparation

Porosity analysis was carried out on mortar samples of approximately 2 grams of mass which were taken from the middle of each cube after the compressive strength test. Several pieces of each crushed cube were dried in an oven at 100°C to remove moisture until a constant weight was achieved. The drying period took approximately 24 hours. After drying, the samples were placed in an airtight bottle until the MIP testing. Silica gel crystals were added to the bottle to absorb any moisture.

- Experimental Parameters

MIP analysis was conducted using following parameters:

i) CD3 dilatometer, which was suggested for measuring pore volume from 0.1 to 500mm^3 and maximum sample size of 12mm in diameter and 40mm in height (**34**).

ii) Total mass of samples ranging between 1.45-1.60 grams.

iii) Mercury surface area of 480 dynes/cm

iv) Contact angle of 141°. The influence of the contact angle used on the cumulative pore volume (CPV) and relative pore volume (RPV) was examined for 4 samples (see Appendix B). Results of these four samples showed that there was a very slight difference in CPV and RPV between using contact angles of either 130° or 141°.

v) Two pieces were used for each MIP analysis. The two pieces were from the total pieces that were obtained after crushing three cubes. The effect of using either one or two pieces for each MIP analysis on CPV and TPV was evaluated (see appendix C). This examination indicated that there was a difference in the CPV whereas there was only a light difference in RPV when either one piece or two pieces was used.

- Repeatability

Repeatability of MIP analysis was examined using two samples obtained from the same batch. MIP analysis was carried out using a contact angle of 141° and 2 pieces per each sample. Figure 3.12 shows CPV and RPV comparisons for two replicate samples In general, the CPV varied insignificantly (no more than 10mm³/g) between the replicate samples. The RPV also appeared to be similar for both samples.

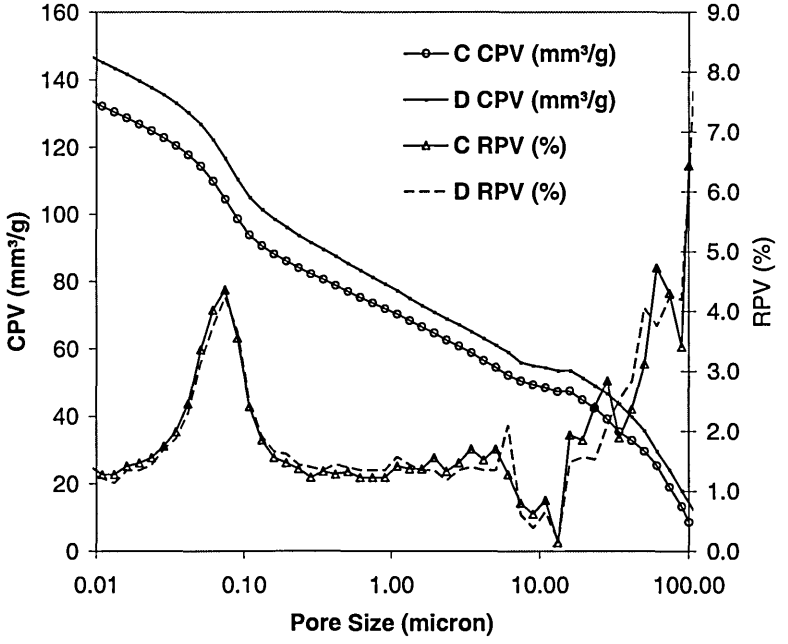


Figure 3.12. Repeatability of MIP analysis for samples that were cast in the same batch.

The repeatability of MIP analysis for sample obtained from different batches was evaluated in order to explain possible change in porosity and pore size distribution of leached samples. MIP analysis was carried out using a contact angle of 141° and 2 pieces per each sample. Figure 3.13 shows CPV and RPV for samples D and E obtained from different batches. There was a significant variation in CPV and RPV for

both samples. For example, the difference in CPV was approximately of 40mm³/g. Although these quantitative variations, CPV and RPV trends were quite similar for both samples.

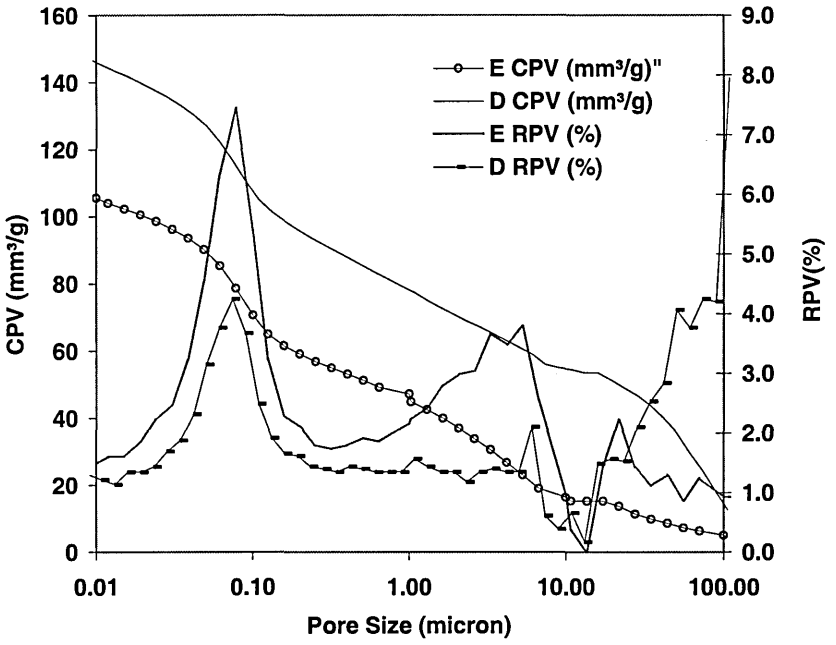


Figure 3.13. MIP analysis for samples that were cast in different batches.

3.5 SAMPLING AND PREPARATION OF MSWI-BA SAMPLES

The inherent heterogeneity of MSWI-BA requires an appropriate sampling method that ensures an adequate level of representative sampling is achieved. Many factors such as household input, incineration operation are involved in the heterogeneity of MSWI-BA samples from a specific incineration facility (**35**).

There are international standards and reports on testing ashes (**36-38**) which can provide guidance on establishing an approach for MSWI-BA collection. The objectives of every particular sample always determine the most practical strategy for collection. The two significant parameters to be considered in any collection are the quantity of material and the frequency. When the purpose of collection is related to utilisation of waste, it may be beneficial to collect large quantities of material with high frequency, whereas for control and regulatory purposes low frequency collection may be the practical strategy (**35**). For this particular research programme, it was impractical to carry out high frequency sampling. Therefore, the sample collection was planned to obtain samples that presented similar chemical and physical properties.

The collection point and quantity of material collected per hour have an influence on the homogeneity of the samples collected. Taking these facts into account, the quantity of MSWI-BA collected per hour was approximately 100kg/h as suggested in ISO 282-

1992 (**39**). The MSWI-BA samples were taken from the cross section of the conveyor belt as recommended in BS EN 932-1 (**40**). The conveyor belt was situated immediately after the water tanks (see Chapter 2) and before the magnetic separator. During collection certain pieces were not subject to selection (e.g. big stones, metal portions and kitchen tools). Having finished the collection, samples were placed in plastic bags and transported to the laboratory. Figure 3.14 shows the collection point at the incineration facility where MSWI-BA was collected on the conveyor belt.

The MSWI-BA samples from the incineration plants contained moisture. The MSWI-BA was dried at 100±2^{0}C for 24 hours to stop further reactions and stored in airtight containers at temperature of 20±1°C and 65±5% RH.

Figure 3.14. MSWI-BA on the conveyor belt

3.6 SAMPLE REDUCTION

The aim of sample reduction is to obtain a laboratory sample that adequately represents the average properties of the whole quantity of materials. Sample reduction was carried out in accordance to BS EN 932-1&2 (**40**,**41**). Appropriate and careful sample reduction strategy is a prerequisite for analysis that will lead to reliable results. Sample reduction needs special care for non-homogenous material as MSWI-BA. For non-homogenous materials it is recommended to increase the number of sample reduction stages and the quantity of material taken for each stage (**40**). These facts were employed with sample reduction of MSWI-BA.

Cement, class M sand, silica sand and all the fractions of MSWI-BA examined throughout the experimental programme were subject to sample reduction. Once a certain amount of those materials was selected from trays or bags, the sample

reductions were carried out by quartering. The sample reduction was conducted in the following sequence:

1. The bulk material subjected to sample reduction was placed on a hard surface.
2. The bulk sample was mixed thoroughly by heaping it up to form a cone and turning it over to form a new cone. This step was repeated four times.
3. The fourth cone was flattened until a uniform thickness of the heap was achieved. The flat heap was divided into four sub-portions, taking two opposite portions and discharging the other two.
4. The process of mixing and quartering were repeated until the required amount for analysis was equal to the sum of the last two sub-portions taken (**42**).

3.7 MIX PREPARATION

Mixes were prepared to examine the mechanical and physical properties, sulfate resistance and leaching behaviour of mortar containing MSWI-BA. The proportion of binder to aggregate was 1:3. The water/binder ratio was constant at 0.50 for all mixes. The binders include cement and fine fractions of MSWI-BA (e.g. grain size below 212μm). Aggregates include class M sand and the coarse fraction of BA. All materials were stored at 20±2^{0}C and 65±5%RH before casting.

3.7.1 Mixing

Mixing was carried out as follows:

1. After weighing, the binder materials (cement & fine fraction of BA) were mixed by hand until homogeneity was achieved.
2. Fine aggregates (class M sand & coarse BA fraction) were placed in the Hobart mixer and mixed for two minutes until homogeneity was achieved.
3. Binders were added to the mixer and mixed with fine aggregates for approximately three minutes.
4. Water was added slowly while mixing took place. The length of mixing was approximately five minutes. The mixing process was interrupted occasionally to remove accumulated material from the paddle and the bottom of the bowl.
5. Once mixing had finished, the mortars were mixed by hand to remove any accumulated material on the base of the mixing bowl and paddle.

3.7.2 Casting

Prior to casting, all the moulds were slightly lubricated with oil. Then, the material was placed in the moulds in three layers, each layer being compacted by hand. Three different size of steel moulds were used:

g) Cubes of dimension 50mmx50mmx50mm for compressive strength, leaching, porosity and saturated density tests.

h) Prisms of dimensions 75mmx75mmx300mm for drying shrinkage test.

i) Prisms of dimensions 40mmx40mmx160mm for sulfate resistance.

3.7.3 Curing

After casting, all samples were placed in a mist curing room at 20°C±1°C and 95%±5% relative humidity for 24 hours. After that de-moulding took place. Mortar samples were cured by three different methods as follows:

j) Curing method A: Mortar samples were placed in water tanks at 20±1°C.

k) Curing method B: Mortar samples were cured in air at 20 ± 2^{0}C and 65±5%RH.

l) Curing method C: Mortar samples were sealed with plastic bags and cured in a mist room at 20±1°C and 95±5% RH.

3.8 DATA ANALYSIS: STATISTICAL INTERPRETATION OF DATA

It is generally agreed that statistics are necessary not only to understand the significance of the data but also to report the results of an investigation in a condensed form for easy interpretation (**43**). Depending on the nature of the investigation, data analysis must be done considering different parameters (e.g. reproductively, repeatability, accuracy). Throughout this experimental programme, the analysis of chemical and physical data has been conducted.

Analysis of chemical data was used mainly to report results of Chapters 4, 5 and 8. The average value of at least three replicate samples was reported. The number of replicate samples was increased up to 5 when a certain procedure or analysis needed to be repeated. The absolute and relative standard deviations were used as an indication of the precision of the analysis. Relative standard deviation was calculated as indicated in Equation 3.8.

$$S(\text{relative}) = \frac{SDEV}{X} * 100 \qquad \textbf{Equation 3.8}$$

where:

SDEV= standard deviation of three identical samples

X= average of three replicate samples

Different methods have been described to identify data which can be rejected from a data set (**17**). In this research programme and particularly in the determination of metals and anions in solutions, data that gave relative a standard deviation higher than 10% was rejected. When it was not possible to achieve a relative standard deviation below 10% for the three replicate samples, more replicate samples were tested.

The results of physical and/or mechanical testing were used mainly in Chapter 4, 6, and 7. For all tests, except drying shrinkage and mercury intrusion porosimetry (MIP) analysis, at least three replicate samples were used to calculate the average value of the data set. Drying shrinkage mean value was calculated from the individual readings of two identical prisms. Porosity and pore size distribution data were generally calculated from a single individual sample, however occasionally, two samples were tested, which were chosen at random.

3.9 CONCLUSIONS

Chapter 3 has described the materials, instruments, techniques and test methods used throughout this research programme. Materials section includes all reagents used to analyse leachate concentration, sulfate solutions used for sulfate resistance test and materials used for making mortar specimens. The instrument section includes a brief description of equipment used such as crushing machine ICP-OES Spectrometer, ion chromatography apparatus. The third section, techniques, describes the main techniques used, ICP-OES, ICP-MS, Ion chromatography and MIP and how testing was carried out. Finally, the last section of Chapter 3 explains the collection and reduction of MSWI-BA and preparation of mortar specimens.

Having explained the methodology and techniques, the next chapter, Chapter 4 presents the chemical and physical properties of various fractions of MSWI-BA.

3.10 REFERENCES

1 BS 12. 1996: Specification for Portland cement

2 BS 882. 1992: Specification for Aggregates from Natural Sources for Concrete

3 BS 1881-116: 1983. Testing Concrete. Method for Determination of Compressive strength of concrete cube

4 BS EN 12390:2000. Testing of Hardened Concrete. Part 5; Flexural Strength of Test Specimens

5 BS 1881-206:1986. Testing Concrete. Part 206: Recommendation for determination of Strain in Concrete

6 BS EN 196-2:1994. Methods of Testing Cement. Part 2: Chemical Analysis of Cement

7 Skoog D.A, Holler F.J. and Nieman T.A. "Principles of Instrumental Analysis". Chapter 10: Atomic Emission Spectrometry. Fifth Edition.1998

8 Meima J.A., van der Weijden R.D., Eighmy T.T. and Comans R.N.J. "Carbonation Process in Municipal Solid Incinerator Bottom ash and their Effect on the Leaching of Copper and Molybdenum". Applied Geochemistry article in press. 2001

9 Andac M. and Glasser F.P. "Long-term Leaching Mechanism of Portland Cement Stabilised Municipal Solid Waste Fly Ash in Carbonated Water". Cement and Concrete Research 29 pp 179-186. 1999

10 Bodenan F., Azaroual M. and Piantone. "Forecasting the Long-term Behaviour of Municipal Solid Waste Incineration Bottom Ash; Rapid Combined Tests". Waste Materials in Construction Wascon 2000. Edited by Woolley G.R., Goumans J.J.J. M. and Wainwright P.J. 2000

11 Skoog D.A, Holler F.J. and Nieman T.A. "Principles of Instrumental Analysis". Chapter 7: Components of Optical Instruments. Fifth Edition.. 1998

12 Yokogawa: Analytical Systems. "HP 4500 ICP-MS Training Manual". Course No. H4035A. 2000

13 Blades M.W. "Applied Spectroscopy". 48, 12-18. 1994

14 Skoog D.A, Holler F.J. and Nieman T.A. "Principles of Instrumental Analysis". Chapter 11: Atomic Mass Spectrometry. Fifth Edition. 1998

15 Skoog D.A, Holler F.J. and Nieman T.A. "Principles of Instrumental Analysis".. Chapter 1: Introduction. Fifth Edition 1998

16 Graham R.C. "Data Analysis for the Chemical Sciences. A Guide to Statistical Techniques." VCH Publishers, 1993.

17 Gary D. Christian. "Analytical Chemistry". Fifth Ed. John Wiley & Sons Inc. 1994

18 Skoog D.A, Holler F.J. and Nieman T.A. "Principles of Instrumental Analysis". Chapter 26: An Introduction to Chromatography Separations. Fifth Edition. 1998

19 Harris D.C. "Exploring Chemical Analysis". Chapter:22: Chromatographic Methods and Capillary Electrophoresis". Second edition. 2000

20 Skoog D.A, Holler F.J. and Nieman T.A. "Principles of Instrumental Analysis". Chapter 28: High-Performance Liquid Chromatography. Fifth Edition.1998

21 BS 7591-1:1992. Porosity and Pore size distribution of Materials. Part 1: Method of Evaluation by Mercury Porosimetry

22 Washburn E.W. "Proceedings of the National Academy of Science". USA, Vol. 7 pp 115-116. 1921

23 Shi D. and Winslow D.N. "Contact Angle and Damage During Mercury". Cement and Concrete Research. Vo.l 15 pp 645-654. 1985

24 Cook R.A. and Hover K.C. "Mercury Porosimetry of Hardened Cement Paste and Concrete Research, 29 pp 933-943. 1999

25 Yates M., Martin-Luengo M.A., Cornejo J and Gonzalez V. "The Importance of Porosity of Mortars, Tiles and Bricks in Relation to their Bonding Strengths".

26 O'Farrell M., Wild S. and Sabir B.B. "Pore size distribution and Compressive Strength of waste Clay Brick Mortar". Cement& Concrete Composites 23 pp 81-91. 2001

27 Olson R.A., Neubauer C.M. and Jennings H.M. " Damage to the Pore Structure of Hardened Portland Cement Pastes by Mercury Intrusion". Journal of the American Ceramic Society, 80, 9, pp 2454-2458. 1997

28 Diamond S. "Mercury Porosimetry. An Inappropriate Method for Measurement of Pore Size Distribution in Cement-Based Materials". Cement and Concrete Research Vol. 30 pp 1517-1525. 2000

29 Neville A.M. Properties of Concrete. Chapter 6 "Strength of Concrete". Fourth and Final Edition. 1995

30 Sing K.S.W. and Yates M. "The Porosity and Permeability of Macro-defect Free Cement". Characterisation of Porous Solids II. Edited by Rodriguez-Reinoso et al. 1991

31 Liu Z. and Winslow D. "Sub-Distributions of Pore Size: A new Approach to Correlate Pore Structure with Permeability". Cement and Concrete Research, Vol. 25, No 4 pp 769-778. 1995

32 Willis K.L., Abell A.B. and Lange D.A. "Image-Based Characterisation of Cement Pore Structure Using Wood's Metal Intrusion". Cement and Concrete Research, Vol. 28, No. 12, pp1695-1705. 1998

33 Laskar A.I., Kumar R. and Bhattacharjee B. "Some aspects of Evaluattion of Concrete through Mercury Intrusion Porosimetry". Cement and Concrete Research Vol. 27 No. 1 pp 93-105. 1997

34 CE Instruments. " Instruction manual Porosimeter Pascual 140& 240".

35 Chandler A.J., Eighmy T.T., Hartlén J., Hjelmar O, Kosson D.S.,Vander Sloot H.A., and Veklow J. "Municipal Solid Waste Incinerator Residues". International Ash Working Group. Studies in Environmental Science 67. Elsevier. 1997

36 SGI. Sampling and characterization of residual Products Interim Report, Part 1- Sampling of residual Product Swedish Geotechnical Institute Report N0 1-253/92. Linköping, Sweden 1993

37 ASTM D 4687-95: Guide for General Planning of Waste sampling

38 ASTM D 3665: Standard practice for random sampling of construction materials, sampling in-place paving materials

39 ISO 282-1992. Conveyor belts-sampling

40 BS EN 932-1:1997 Tests for general properties of aggregates. Methods for Sampling

41 BS EN 932-1:1999 Tests for general properties of aggregates. Methods for Reducing Laboratory Samples

42 ASTM D 346: Practice for Collection and Preparation of Coke. Samples for laboratory Analysis

43 BS 2846-1 1991. Guide to Statistical interpretation of data. Part 1: Routine analysis of quantitative data

CHAPTER 4: CHEMICAL AND PHYSICAL PROPERTIES OF UNBOUND MSWI-BA

4.1 INTRODUCTION

The examination of chemical and physical properties of municipal solid waste incinerator bottom ash (MSWI-BA) is the first stage to identify its potential utilisation. The literature review on chemical and physical properties of MSWI-BA indicated that these properties can vary widely even for the same incineration facility due to the heterogeneity of MSW input and operational conditions. Some new incineration plants pre-treat the MSWI-BA prior to utilisation or disposal, with a view to improving MSWI-BA engineering properties and environmental impact, whereas other incineration plants transport and send the MSWI-BA to landfill sites directly from the quenching tank. Thus, a wide variation of MSWI-BA samples can be found (**1**).

The examination of physical properties includes a visual observation, the determination of the water content, bulk density, specific gravity and sieve analysis. Density, specific gravity and particle size distribution are important parameters when considering the homogeneity (e.g. shape of particles), porosity of the bulk, and the degree of compaction of materials. In general a uniform gradation indicates potential use of the material as an aggregate substitute (**2**). The examination of chemical properties includes generally the determination of the pH profile, inorganic composition, loss on ignition.

This chapter examines the physical and chemical properties that were considered relevant for assessing the usage of MSWI-BA in cement-based systems. These are water content, density, particle size distribution, pH, inorganic composition and loss on ignition (LOI).

4.2 VISUAL EXAMINATION

In general, a visual observation of MSWI-BA gives an idea of its grains size and also provides an assessment of the relative efficiency of the combustion process. The visual observation of the MSWI-BA from the incineration plant in Nottingham showed a high amount of glass, ceramics, ferrous and non ferrous metals, slag materials and large stones. In addition, a low quantity of unburned papers and gardening residues were present. A wide grain size distribution was observed for ceramic materials. Figure 4.1 shows four photographs of different fractions of MSWI-BA. Figure 4.1 -a shows raw fraction of MSWI-BA which consisted of MSWI-BA as received from incineration plant without large pieces (e.g. stones). Figure 4.1 -(b), (c) and (d) show three grain size fractions of MSWI-BA after being dried at 100°C for 24 hours and dividing in fractions. The particle diameter (∅) of these fractions were ∅<212μm, 212μm<∅<2.36mm and

2.36mm∅<5.00mm. The visual observation of the MSWI-BA reveals the absolute necessity of sorting this bottom ash into fractions. These fractions will undergo specific treatment depending on further applications.

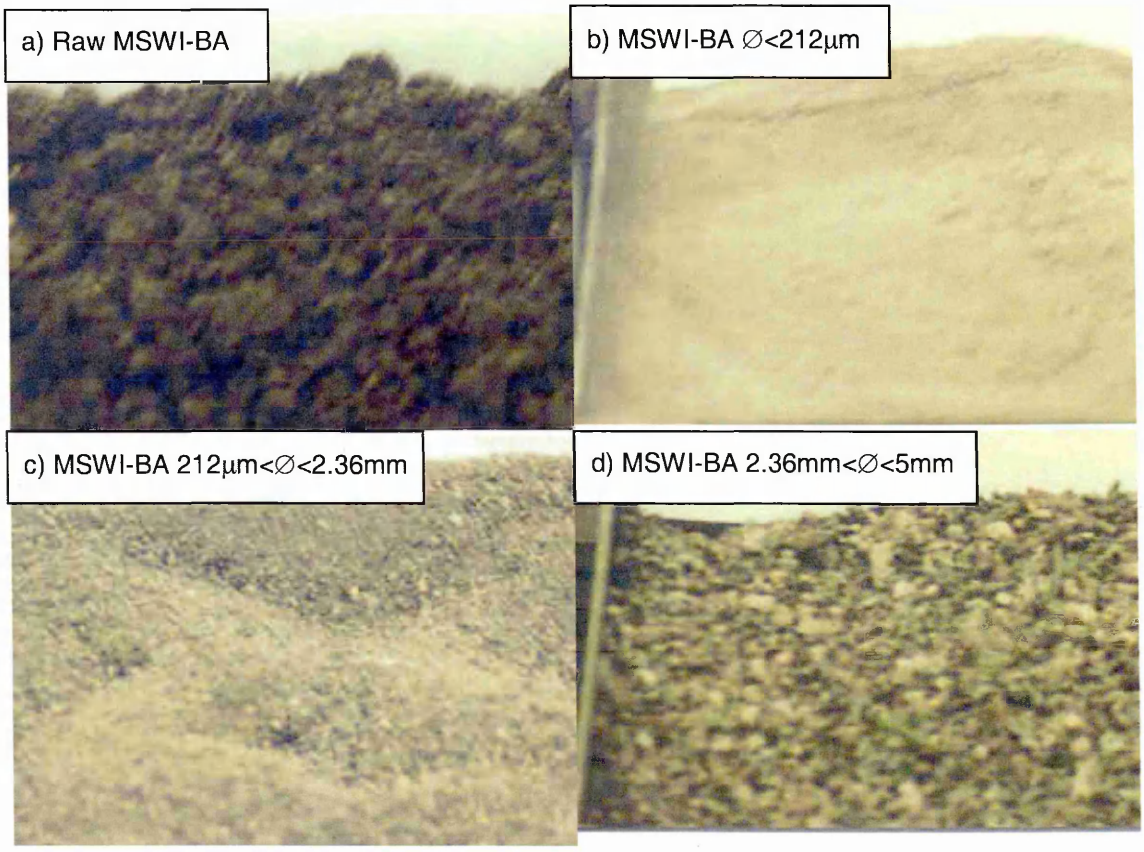


Figure 4.1: MSWI-BA photos; (a) Raw MSWI-BA; (b) MSWI-BA ∅<212μm; (c) MSWI-BA with 212μm<∅<2.36mm and (d) MSWI-BA 2.36mm<∅<5.mm

4.3 EXPERIMENTATION

4.3.1 Materials

The materials tested were four fractions of MSWI-BA; 1) raw MSWI-BA as received from incineration facility without large particles; 2) MSWI-BA fraction consists of particles with diameters below 2.36mm (∅<2.36mm). This fraction was ground in a hammer mill for 3 minutes for investigating the influence of particle size on chemical composition; 3) MSWI-BA fraction with particle diameters below 212μm (∅<212μm); 4) MSWI-BA fraction with particle diameter between 212μm and 2.36mm (212μm<∅<2.36mm).

A Portland cement and class M sand were also included in physical and chemical characterisation of MSWI-BA for comparative purpose because two fractions of MSWI-BA were used to partially replace cement and sand.

4.3.2 Testing

4.3.2.1 Water Content

Water content test was determined in accordance with BS EN 1097-5 (**3**) and BS 812 part 109 (**4**).The water content consisted of drying several test samples of MSWI-BA in a ventilated oven at 100±5^{0}C until a constant weight was achieved. After drying, test samples were left to cool in a desiccator, filled with silica gel, for approximately 3 hours. The water content is determined as the difference between the wet and dry weights. Water content was determined for six samples and the average was reported.

4.3.2.2 Density

Test methods used to determine particle density and bulk density are based on specifications and apparatus requirements given in BS 812-2 and BS EN 1097 part 3 and part 7 (**5-7**). For each density test, three identical samples were used. The samples for the density test were taken from approximately one kg of each material which was subjected to sample reduction procedures.

For the materials examined, three identical samples were tested. Particle density was obtained by averaging the three test samples and reported to the nearest 0.01. Any individual result that differed by more than 0.02 was not considered as recommended in BS 812-2 (**5**). The average bulk density was calculated to the nearest 0.01 Mg/m^3 and any value that differed more than 0.05 Mg/m^3 was not considered for calculating the average (**5**).

- Particle Density

The particle density or apparent gravity density is calculated by the ratio of the dried mass of the sample to the mass of water occupying a volume equal to that of the sample which includes the impermeable pores. The particle density was determined as follows:

1. Test samples of approximately 200 grams in weight were dried at 105±5°C until constant weight was achieved. This took around 2 to 3 hours.
2. After drying, samples were left to cool in a desiccator under room conditions. In the meantime, the calibration of the density container, known as a pycnometer, and determination of density of kerosene were carried out as follows:

a) The calibration of pycnometer consisted of calculating the true volume (V_k) of pycnometer as indicated in Equation 4.1. The dried pycnometer weight was recorded (m_0), and then filled up with distilled water. Next, the pycnometer was

immersed in a water bath, which was capable of maintaining a temperature of 25±0.1°C, for 1 hour. After immersion the weight was recorded (m_w).

$$V_k = \frac{m_w - m_0}{\rho_w} = \qquad \textbf{Equation 4.1}$$

where:

V_k= volume of kerosene

m_0 = mass of the pycnometer empty

m_w= mass of the pycnometer full of water

ρ_w= density of water which is equal to 1g/ml

b) The density of the Dilatometric liquid, re-distilled kerosene with a boiling range between 180°C and 280°C, was determined by repeating the above procedure and using Equation 4.2;

$$\rho_k = \frac{m_k - m_0}{m_w - m_0} \qquad \textbf{Equation 4.2}$$

where:

m_k= mass of the pycnometer density bottle full of kerosene

ρ_k= density of kerosene

3. After cooling, the sample was added into the empty pycnometer using a small funnel, so as to fill approximately one-third of the bottle, and then its weight was recorded ($m_{sol} + m_0$).

4. Once the pycnometer had been filled with kerosene it was then immersed in a water bath for not less than one hour. Finally, the weight of the pycnometer, solid and kerosene were recorded and particle density (ρ_p) was calculated using the following equations:

$$V_{sol} = V - V_K \qquad \textbf{Equation 4.3}$$

$$\rho_p = \frac{m_{sol} - m_0}{V_{sol}} \qquad \textbf{Equation 4.4}$$

$$\rho_p = \left[\frac{m_{sol} - m_0}{\left(\frac{m_w - m_o}{\rho_w}\right) - \left(\frac{m_T - m_{sol}}{\rho_k}\right)} \right] \qquad \textbf{Equation 4.5}$$

Where:

V= total volume

m_{sol}= mass of the density bottle and solid added

m_T=mass of the density bottle, the solid and kerosene

- Bulk Density

Bulk density was determined using methods A and B.

a) Method A

In method A, bulk density was calculated by the ratio of the dried mass of sample to the wet volume of sample in kerosene. This method was used for samples of cement, class M sand and fractions with $\varnothing$<212μm and with 212μm<$\varnothing$<2.36mm. Sampling, drying and cooling procedures were the same as that described above for particle density (steps 1, 2 and 3). Once test samples had cooled, 10±0.01grams of solids and approximately 25ml of kerosene were placed into a graduated glass cylinder, which had 1ml divisions. To ensure that the solid was in complete suspension the cylinder was inverted and shaken several times (at least four times), while adding more kerosene. Finally, the cylinder was left to settle for 6 hours before recording the bulk volume of the solid to nearest millilitre.

The bulk density (ρ_b) for each test sample was calculated to the nearest 0.01 Mg/m^3 using Equation 4.6:

$$\rho_p = \left[\frac{m - m_o}{V}\right] \qquad \textbf{Equation 4.6}$$

Where:

m= mass of samples which was equal to 10g

m_o= wet mass of samples before drying

V= volume recorded from the graduated cylinder

b) Method B

In method B, the bulk density is calculated by the ratio of the dried mass of test sample to the volume of a container. The volume of the container was determined previously, by filling it with distilled water at standard conditions. This method was used to determine the bulk density of class M sand and the MSWI-BA fraction with a particle diameter 212μm<$\varnothing$<2.36mm. This test consisted of filling a container with dried sample (105±5°C), taking care to approximate the volume of the sample to the volume of the container. The volume of the container was previously calculated by determining the maximum mass of distilled water to fill the container. Care was taken to avoid any compaction whilst samples were being added and to remove the surplus sample from above the top of the container, without compacting any part of the upper surface of the sample. The bulk density is directly calculated by dividing the mass of sample by the volume of the container as shown below;

$$\rho_b' = \left[\frac{m - m_o}{V}\right]$$ Equation 4.7

m= dried mass of samples to fill the container completely.

m_o= wet mass of samples before drying

V= volume of container

4.3.2.3 Sieve Analysis

The sieve test was carried out in accordance with BS 812: Part 103 (**8**), using 500 g of test sample for each test. MSWI-BA samples were screened for approximately 18 minutes and the material retained on each sieve was weighed to determine the retained proportion of each grain size.

Sieve analysis was carried out for each collection to evaluate possible difference in particle size distribution between each collection. Prior to testing, raw MSWI-BA was dried at 100±5^{0}C for 24 hours and subjected to sample reduction stage. Sample reduction was carried out in a selected number of trays chosen at random. Sample reduction is described in detail in Chapter 3.

4.3.2.4 Determination of pH

The test methods used to determine the pH followed the recommendations given in ASTM D-4980-89 (**9**). The test consisted of placing MSWI-BA samples in different volumes of water. Table 4.1 summarises the three procedures that were carried out for the different samples examined. The duration for all procedures was 24 hours. For two of the procedures used, agitation was required.

Table 4.1. Parameters for pH test

	Procedure 1	Procedure 2	Procedure 3
Sample mass (g)	10	10	10
Water volume (ml)	100	150	100
Agitation	Magnetic stirred	Magnetic stirred	No agitation
Duration (days)	24	24	24

In order to assess the pH profile beyond to 24 hours, a new test series was conducted keeping the parameters that were set in procedure 3 (i.e. no agitation and s/l ratio 10). Thus, for every test MSWI-BA samples were mixed with distilled water and left to settle. Two different weights of samples were tested (20 and 50 grams), keeping the same solid/ water ratio.

The pH-meter was calibrated every day before testing using buffer solutions. To reduce possible interference from variation of temperature, release of suspended material, a pH-meter with compensation of temperature was used and readings were only recorded once samples had been settled previously.

4.3.2.5 Inorganic Composition

Sample preparation for inorganic determination needs careful consideration to minimise potential variability due to the intrinsic heterogeneity of MSWI-BA. The MSWI-BA consists of a mixture containing a wide range of elements. Elements may be presented in various phases. This variety of elements and phases makes it difficult to determine each individual element. Therefore, it was decided to determine the major and minor elements of MSWI-BA employing X-ray fluorescence spectrometry. Major elements include Ca, Si, Al, Fe, Mg, K, Na, S and Cl. Minor elements include Zn Pb, Mn, Ba, Cu, Sn, Cr, and Ni.

For the determination of chemical composition, semi-quantitative and quantitative analyses were carried out. Each test method requires different sample preparation. These were as follows:

a) Method 1: semi-quantitative analysis required pressed pellets of the samples. 8 grams were compacted in a mill for 1 minute to make pellets, which were placed into X-ray fluorescence spectrometer.

b) Method 2: quantitative analysis required fused samples. The fusion procedure includes the following stages:

1. One gram of sample was mixed with 10g of dilithium tetraborate. The mixture was weighed with an accuracy of 0.0001g.
2. The mixture was fused at 1250^{0}C for 12 minutes.
3. The fused mixture was cooled for half and hour.
4. Finally samples were analysed in the spectrometer.

The examination of inorganic composition of MSWI-BA was carried out for the following experimental series:

1. Series 1 consisted of the determination of major elements of MSWI-BA fractions with particle diameters (∅) below 75μm, 150μm, 212μm, 300μm, 600μm and 1.18mm, and particle with 212μm<∅<2.36mm, 2.36mm<∅<5mm and ground MSWI-BA fraction using method 1 (semi-quantitative). For MSWI-BA fraction with 212μm<∅<2.36mm and 2.36mm<∅<5mm, three replicate samples were subjected

to testing and the average was reported. However, for fractions with particle diameter lower than 1.18 mm only one sample was tested, because they exhibited good consistency and homogeneity of results after some identical samples were tested.

2. Series 2 included the determination of major elements in MSWI-BA fractions with Ø<212μm, 212μm<Ø<2.36mm and ground MSWI-BA using method 2.
3. Series 3 consisted of determining of minor elements in MSWI-BA fractions with Ø<212μm, 212μm<Ø<2.36mm and ground MSWI-BA using method 2.
4. Series 4 consisted of the determination of major elements for fractions of MSWI-BA with Ø<212μm and ground MSWI-BA that were obtained from each collection. The chemical composition was determined using method 2.

4.3.2.6 Loss-on-ignition

The loss on ignition is expressed as the percentage of mass reduction which occurred by igniting a sample at a specific temperature. The procedure used was similar for the different samples tested. The only difference was the temperature of ignition, which was 775±25°C, as recommended in BS 3797 (**10**) for aggregates such as class M sand with Ø<2.36mm and MSWI-BA with 212μm<Ø<2.36mm and 975±25°C, as recommended in BS EN 196-2 (**11**) for cement and MSWI-BA with Ø<212μm.

Approximately 100grams of each material were dried at 105±5°C until a constant mass was achieved. The mass was then reduced to approximately 25 grams and then ground until passing through a 150μm test sieve. The sample weight (m_0) was 2 grams with an accuracy of 0.001g. Samples were placed on a dish which had been ignited previously. The covered dish was then placed in a muffle furnace either for 2 hours or for 15 minutes when aggregates or cementitious materials were tested. Finally test samples were allowed to cool in a desiccator under room conditions and then weighed. In order to avoid the loss of material by exposition during the ignition process, the dish containing the test sample was covered during the first 5-7 minutes. The % loss on ignition was calculated by the equation shown below;

$$\%LOI = \left[\frac{\Delta m}{m_0} * 100\right] \qquad \textbf{Equation 4.8}$$

Were:

Δm=loss in mass is the difference between original mass and mass after ignition

m_0=original mass

4.4 RESULTS

4.4.1 Water content

Results of MSWI-BA water content are calculated in two different forms: 1) Method I, water is expressed as the mass of the water divided by the mass of dry material; 2) Method II, water content is expressed as the mass of the water divided by the total wet mass the sample. Both water contents are expressed as a percentage. Table 4.2 shows the average value of the six samples tested for each collection of MSWI-BA.

Table 4.2: Water contents of MSWI-BA

Collections	Method I (%)	Method II (%)
1	21.18	12.92
2	35.28	17.39
3	21.79	14.61
Average	26.08	14.97

Collection 1 and 3 exhibited similar water contents. However, collection 2 gave a higher content than the others. The difference in water content for the different collections could be attributed to the variation in operation in the incineration plant.

4.4.2 Density

Particle density and bulk density have been examined to show the degree of compliance of MSWI-BA with standards specifications given for other materials used in construction.

Table 4.3 presents the values of particle density and bulk density for the fractions of MSWI-BA with $\varnothing$ <212μm and 212μm<$\varnothing$<2.36mm. Also, the density of cement and class M sand are included in the table for comparison purpose. Particle and bulk densities for the fraction of MSWI-BA with $\varnothing$<212μm were 17% and 25% respectively lower than those for cement. The particle densities of MSWI-BA with 212μm<$\varnothing$<2.36mm and class M sand were slightly different whereas their bulk densities were significantly different. The bulk density of MSWI-BA with 212μm<$\varnothing$<2.36mm was about 40% lower than that for class M sand.

Table 4.3. Particle and Bulk Densities for two fractions of MSWI-BA, cement and class M sand

Materials		Particle density		Bulk density (Mg/m^3)			
				Method A		Method B	
Binder	Ø <212μm	2.270	±0.006	0.604	±0.012	-	-
	Cement	3.010	±0.005	0.727	±0.013	-	-
Aggregate	212μm<Ø<2.36mm	2.335	±0.007	0.960	±0.013	0.926	±0.009
	M Sand Ø<2.36mm	2.610	±0.019	1.559	±0.036	1.494	±0.011

4.4.3 Sieve Analysis

It was observed that a certain quantity of fine particles was sometimes adhered to coarse particles during the sieve test. This effect would slightly alter the true percentages of coarse and fine particles. However, the separation of coarse and fine particles (e.g. using a pre-washing stage) prior to sieving was not possible due to the high solubility of MSWI-BA fine particles as a result of the chemical composition (CaO, $Ca(OH)_2$).

Grading curves for samples obtained from different collections are provided in Figure 4.3. The vertical axis represents the cumulative percentage passing and the horizontal axis shows the sieve opening plotted on a logarithmic scale. The sieve analysis of the three collections was similar. A slight difference in percentage passing was observed for grains with diameter below 600μm. There was a gradual increase in the percentage passing from grains sizes up to 1.18mm and after that a significant increase in grading slope was observed. Particles with grain diameters below 2.36mm represent around 40% of the MSWI-BA.

Figure 4.3 shows the sieve analysis for class M sand and the fraction of MSWI-BA with Ø<2.36mm. The sieve grading of the MSWI-BA with Ø<2.36mm is the average of sieve grading from the samples of Figure 4.2. The limits for grading class M fine aggregates set down by BS 882 (**12**) are also shown in the figure. The class M sand with diameter of particles below 2.36mm is similar to the upper limit given in BS 882, whereas the grading curve for MSWI-BA with Ø<2.36mm is between upper and lower limits.

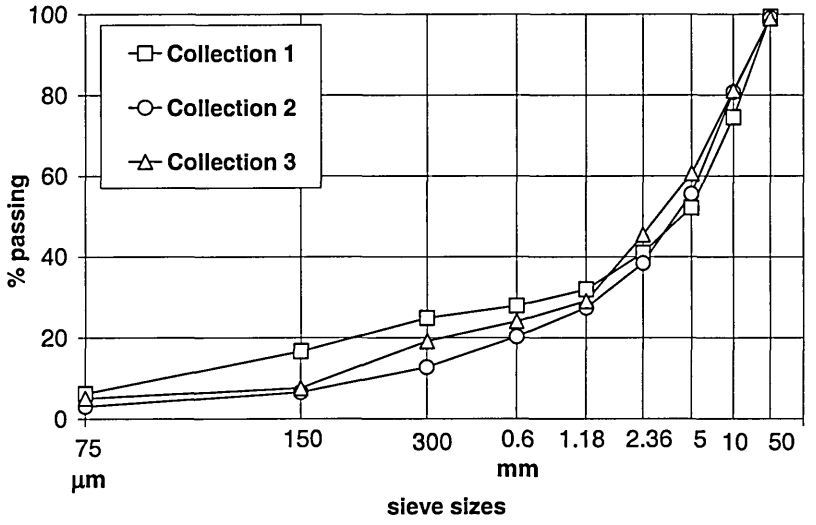


Figure 4.2. Sieve analysis of raw MSWI-BA

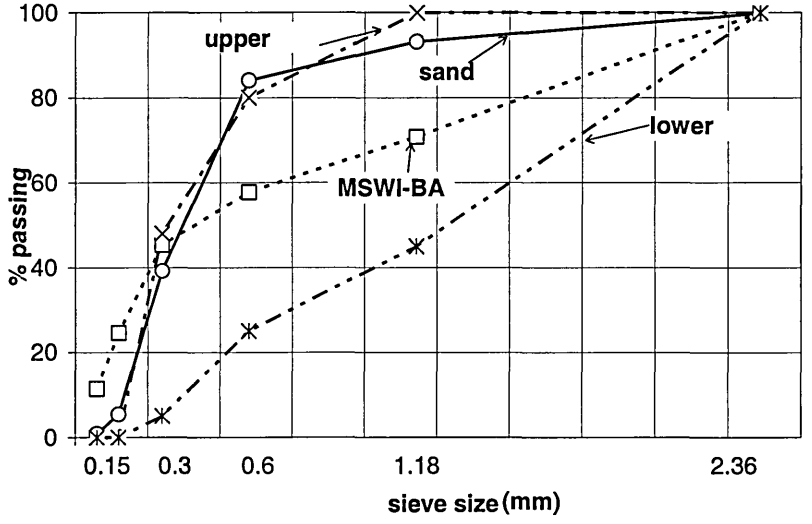


Figure 4.3. Comparison of sieve analysis of class M sand with MSWI-BA

4.4.4 pH Profile

The determination of the pH of MSWI-BA was conducted to assess possible toxicity and to compare the pH values for different fractions of MSWI-BA. Three replicate samples were used to report the average. No significant standard deviations were observed between the three identical test samples. Figure 4.4 shows the pH values observed for the three procedures conducted over 24 hours.

In general, the pH varied from 10.5 to 13 for the different fractions of MSWI-BA examined. The raw MSWI-BA samples and the coarse fraction of MSWI-BA (212μm<∅<2.36 mm) exhibited almost identical pH values regardless on the pH procedure used. The fine MSWI-BA fraction (∅<212μm) always exhibited higher pH than the raw and the coarse fraction of MSWI-BA. This suggested that the former

probably had higher content of CaO than the other fractions examined. Using procedure 1 (agitation and s/l =10), the difference in pH increased between the finer fraction and the other two fractions (raw MSWI-BA and 212μm<Ø<2.36 mm). The decrease in pH during the first 24 hours for all MSWI-BA fractions using procedure 1 was associated with the carbonation reaction and possible precipitation of hydroxides. Carbonation is facilitated by the agitation and a lower solid/liquid ratio (s/l). Each fraction of MSWI-BA examined gave similar pH values using Procedure 2 and 3. This suggested that agitation and higher s/l ratio of procedure 2 was balanced with no agitation and lower s/l ratio used in procedure 3.

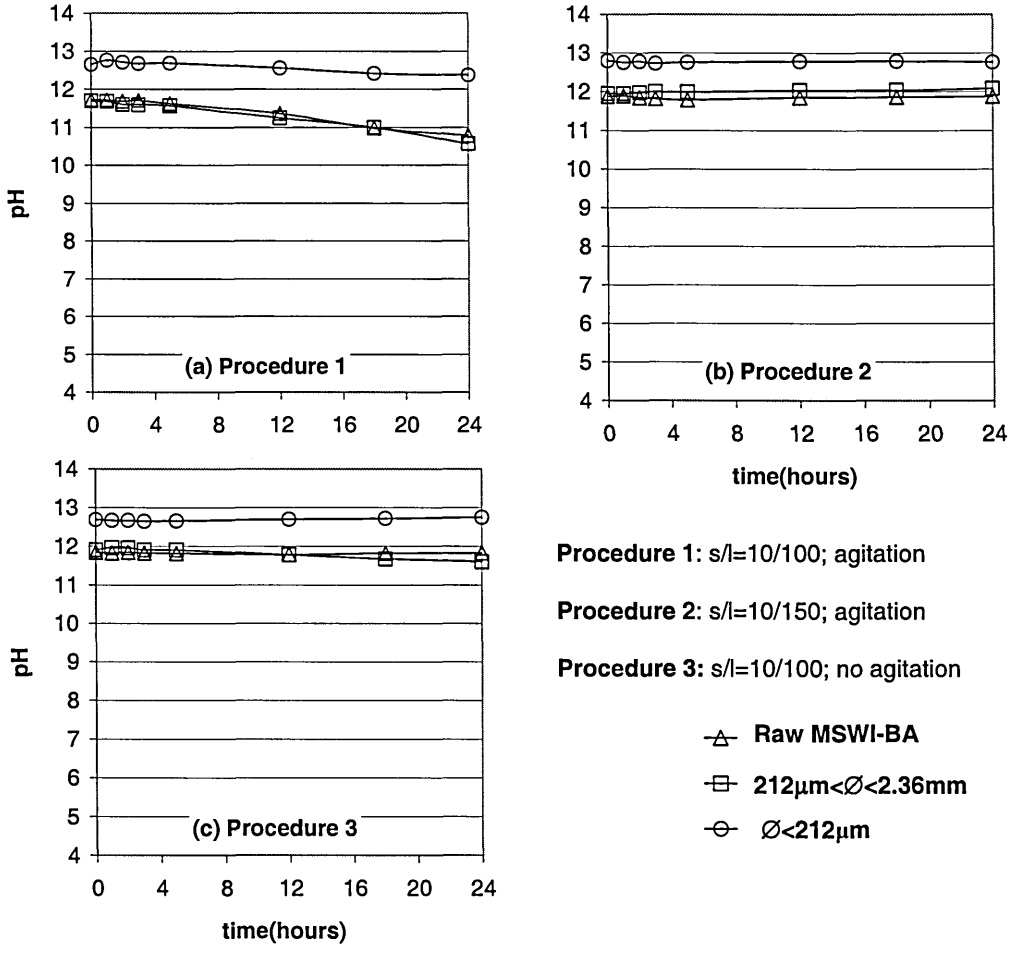


Figure 4.4. pH profile during 24 hours (a) procedure 1, (b) procedure 2, (c) procedure 3

Figure 4.5 shows the pH profile for same fractions of MSWI-BA during the first 300 hours in contact with water. Figure 4.5-a shows the pH profile using a solid/liquid ratio of 20 grams of solid in 200ml of deionised water. Figure 4.5-b shows the pH profile using 50grams of solid in 500ml of deionised water. During pH testing, the carbonation reaction took place because samples were in contact with atmospheric air; therefore, a reduction of pH was expected due to the formation of less soluble compounds (e.g. calcite). Raw samples of MSWI-BA exhibited the same pH profile using both volumes of solution, whereas, the pH profile for fractions of MSWI-BA with diameter below

212µm and with diameter between 212µm and 2.36mm were slightly different. The lower pH of MSWI-BA fractions with ∅<212µm and 212µm<∅<2.36mm using 200ml of volume solution compared with that of 500ml was not clearly explained. Using the ratio 50/500, the effect of evaporation with test duration is reduced, and more accurate pH reading can be measured. Raw samples and samples with a diameter ranging from 212µm and 2.36mm showed a decrease in their pH approximately one unit of pH scale during 300 hours in contact with water. The pH of the finer fraction was nearly constant at 12. The high and almost constant pH for fine fraction of MSWI-BA indicated high content of alkali hydroxides (e.g. $Ca(OH)_2$, whereas, the coarse fractions of MSWI-BA (raw and 212µm<∅<2.36mm) possess mineral compounds (e.g. SiO_2) which do not contribute largely to pH value.

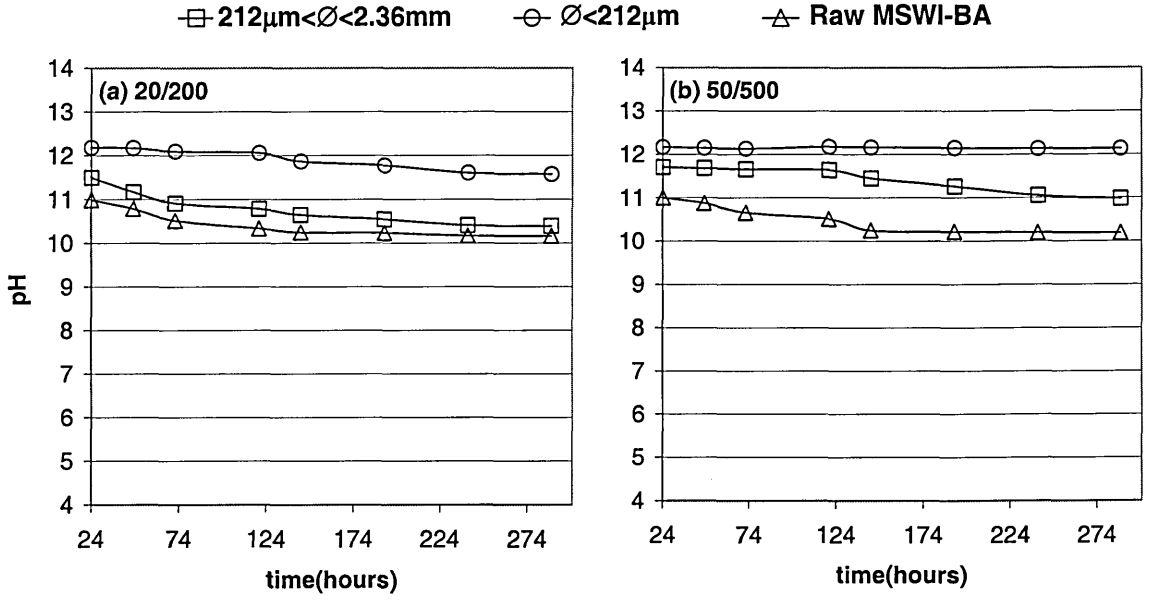


Figure 4.5. pH profile of MSWI-BA during 300 hours

4.4.5 Inorganic Composition

The determination of inorganic composition of MSWI-BA was conducted to predict its potential uses and to evaluate the presence of toxic elements.

Table 4.4 shows the contents of major oxides for fractions of MSWI-BA with diameter below 75µm, 150µm, 212µm, 300µm, 600µm and 1.18mm. Concentrations of oxides were determined using the semi-quantitative procedure (Method 1, see section 4.3.2.5). Silicate, lime and sulphur oxide, expressed as SO_3, contents varied as a function of grain diameters. Silicate and Fe_2O_3 contents increased from approximately 25% to 30.5% and from 4% to 5.5% respectively with the increase in particle size, whereas, lime and SO_3 contents decreased from 35.5% to 29% and from 9.5% to 8% respectively. The progressive increase of CaO in the finer fraction is almost mainly due

to the fine lime particles in the MSWI-BA deriving mainly from paper. The contents of Na_2O, K_2O, MgO, chlorides and Al_2O_3 were almost similar for all fractions of MSWI-BA with diameters below 1.18mm. The fractions of MSWI-BA with diameters below 75μm, 150μm and 212μm exhibited similar chemical composition regarding the major component contents.

Table 4.4. Major Element Contents in Fine Fractions of MSWI-BA (Method 1)

	Contents in %								
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	Cl
Ø<75μm	35.4	25.2	14.5	3.9	3.0	2.6	1.5	9.3	1.3
Ø<150μm	34.3	26.1	14.5	4.0	2.9	2.5	1.6	9.2	1.3
Ø<212μm	33.6	26.3	14.8	4.0	2.9	2.7	1.6	9.2	1.3
Ø<300μm	30.7	29.5	14.9	4.3	2.9	2.8	1.6	8.5	1.2
Ø<600μm	30.6	29.6	14.9	4.4	2.9	2.9	1.6	8.3	1.2
Ø<1.18mm	29.0	30.6	14.7	5.6	2.8	2.8	1.7	7.9	1.2

Table 4.5 provides the major element contents for MSWI-BA with 212μm<Ø<2.36mm and 2.36mm<Ø<5mm. These contents were determined using the semi-quantitative procedure (Method 1). It was observed that the contents of MgO, K_2O and Al_2O_3, were similar for both fractions of MSWI-BA, whereas, the other contents vary notably. MSWI-BA with particle diameters ranging from 212μm to 2.36mm exhibited higher contents of CaO, Fe_2O_3, SO_3, and Cl than the fraction with grain diameter between 2.36mm and 5mm. Coarser fraction (2.26<Ø<5mm) presented higher contents of Na_2O and SiO_2.

Table 4.5. Major element contents in coarse fractions of MSWI-BA (Method 1)

	Contents in %								
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	Cl
212μm<Ø<2.36mm	22.2	38.99	11.9	8.6	2.5	2.5	3.1	5.5	1.1
2.36mm<Ø<5mm	14.6	55.4	11.0	5.3	2.7	2.1	5.5	2.1	0.5

Table 4.6 provides a comparison of oxide concentrations using the pressed (method 1) and the fused (method 2) methods (see section 4.3.2.5). The fractions of MSWI-BA examined included particles with Ø<212μm, 212μm<Ø<2.36mm and ground fraction of MSWI-BA. The ground fraction consisted of particles with diameters below 150μm.

Lime and silicate contents differed widely depending on the method used. This difference between both methods can be attributed to the fact that CaO particles were on the surface of SiO_2 grains. Hence, in pressed samples, the particles of SiO_2 were hidden behind CaO particles and, therefore readings of SiO_2 contents were lower than true values. However, when samples were fused, CaO particles were separated from SiO_2 grains and the X-ray fluorescence spectrometer could identify all SiO_2 content presented in samples.

Table 4.6: Comparison of oxide concentrations using methods 1 and 2

	Oxide Contents (%)					
	Ø<212μm		212μm<Ø<2.36mm		Ground Ø<2.36mm	
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
CaO	33.6	22.8	22.2	12.9	18.3	15.3
SiO_2	26.3	35.2	39.0	49.8	27.8	45.6
Al_2O_3	14.8	10.9	11.9	11.8	19.9	11.2
Fe_2O_3	4.0	4.3	8.6	10.3	3.0	9.7
MgO	2.9	2.3	2.5	2.3	7.4	2.0
K_2O	2.7	1.7	2.5	1.9	1.3	1.6
Na_2O	1.6	1.6	3.1	2.7	6.8	2.2

Contents of Al_2O_3 were higher using method 1 than 2 for fractions with Ø<212μm and ground fraction, whereas contents of Al_2O_3 for the fraction with 212μm<Ø<2.36mm were similar using methods 1 and 2. The higher contents of Al_2O_3 for fractions with Ø<212μm and ground using method 1 compared with 2 may be attributed to same effect reported earlier for CaO. However, the similarity of Al_2O contents for fraction with 212μm<Ø<2.36mm was not clear. For all fractions of MSWI-BA, the concentrations of Al_2O_3 were similar when the fused method was employed.

Fractions of MSWI-BA with particle diameters Ø<212μm and 212μm<Ø<2.36mm exhibited similar contents of Fe_2O_3, MgO, K_2O and Na_2O using the two methods. In the ground fraction, the Fe_2O_3 contents exhibited a similar trend to silicate whereas MgO, and Na_2O exhibited a similar trend to lime.

In general, it was observed than the determination of oxide compositions for major elements was more accurate using method 2 than 1 due to the fusion of samples prior to analysis. The fusion of samples improves detection of major elements by increasing fineness of samples and reducing hidden effects.

Table 4.7 shows the concentrations of minor elements for different fractions of MSWI-BA with Ø<212μm, 212μm<Ø<2.36mm and ground fraction. The concentrations are expressed as gram of element per kg of MSWI-BA samples. The determination of metals was carried out using method 2 (fused samples). MSWI-BA with diameter Ø<212μm presented higher concentrations of Zn, Cu, Pb, Mn and Ba compared with the other fractions examined. For all fractions tested, Zn content was highest than other elements. XRF spectrometry technique may not be suitable for accurate determination of elements with low concentrations. However, these concentrations were considered to determine the maximum amount of metal that can be leached.

Table 4.7. Concentration of minor elements (expressed as g/kg of MSWI-BA) (Method 2)

	Ø<212μm	212μm<Ø<2.36mm	Ground Ø<2.36mm
Zn	3.4	1.9	2.6
Pb	1.7	<1	1.4
Mn	1.4	1.0	<1
Ba	1.2	<1	1.0
Cu	1.2	<1	1.0
Sn	<1	<1	<1
Cr	<1	<1	<1
Ni	<1	<1	<1

Table 4.8 shows the composition of major elements, expressed in percentage, for MSWI-BA with Ø<212μm and the ground fraction for samples obtained from different collections. In general, the content of major elements did not vary largely for each collection day. The contents of silicate and lime were slightly different from different collections. The difference in CaO and SiO_2 contents was higher for the fraction with Ø<212μm compared with the ground fraction. All samples showed that the mayor oxide content were CaO, SiO_2 and Al_2O_3.

Table 4.8. Composition of major elements, expressed in %, for different collection

	Ø<212μm			Ground MSWI-BA		
	Collec. 1	Collec. 2	Collec. 3	Collec. 1	Collec. 2	Collec. 3
CaO	30.3	34.2	36.4	18.1	16.8	20.3
SiO_2	24.3	26.4	28.2	24.1	30.3	28.9
Al_2O_3	15.0	15.1	14.6	18.9	20.2	19.9
Fe_2O_3	4.0	4.1	4.0	3.3	2.7	3.0
MgO	2.9	2.9	2.9	9.0	7.2	6.9
K_2O	2.6	2.9	2.5	1.3	1.3	1.3
Na_2O	1.5	1.7	1.6	4.8	9.0	6.5
SO_3	9.7	9.1	8.6	7.0	5.6	6.0
Cl	1.4	1.4	1.1	1.1	1.0	1.1

4.4.6 Loss on Ignition

Loss on ignition (LOI) was determined to predict content of organic substances in MSWI-BA samples. Figure 4.6 shows LOI, expressed as percentage, for fractions of MSWI-BA with Ø<212μm and 212μm<Ø<2.36mm. The LOI of cement and class M sand with diameter Ø<2.36mm are also presented. Both MSWI-BA fractions possessed higher LOI than cement and natural sand. The finer fraction of MSWI-BA exhibited the highest LOI, which suggested that its organic content is higher than the other materials examined. The higher LOI of finer fraction can also derive from the higher content of $CaO/CaCO_3$, which produce great LOI.

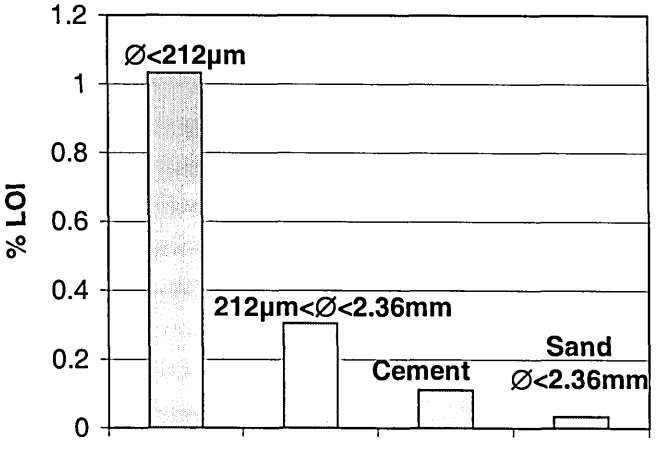


Figure 4.6. LOI for two fractions of MSWI-BA, cement and class M sand

4.5 DISCUSSION OF RESULTS

4.5.1 Properties of Raw MSWI-BA

Raw MSWI-BA required a drying stage to divide MSWI-BA into different grain distributions. Water contents ranging from 25% to 45% are commonly reported for MSWI-BA (**13- 15**). The lower water contents reported for MSWI-BA in this programme of research compared with other authors may be associated with the type of quenching stage carried out to cool the ash in the incineration facility studied. The decrease in water content for MSWI-BA is associated with the need to reduce further leaching reactions in landfill sites.

The grading analysis of MSWI-BA, which is provided in Table 4.9, showed that MSWI-BA contains higher percentage of fines compared with a typical "MSWI BA" (**16**). Since high level of fines can be associated with a great freezing-thaw susceptibility it can be expected that freezing-thaw performance of raw MSWI-BA is not as good as other MSWI BA (**1,2**).

Table 4.9. Comparison of sieve analysis for MSWI-BA and for typical MSWI-BA

	% Percentage passing	
Sieve size	**MSWI-BA**	**MSWI Bottom Ash (16)**
50mm	100	N/A
10mm	97-100	55-100
5mm	45-60	30-55
2.36mm	39-45	20-30
1.18mm	27-32	18-20
600μm	20-28	6-18
300μm	12-24	6-10
150μm	7-17	0-6
75μm	3-6	N/A

In order to compare sieve analysis for MSWI-BA with soil, three parameters were determined; the uniform coefficient, U, the coefficient of curvature, C, and the frost susceptibility (**17**). The uniform coefficient is defined as the ratio of the particle diameter at 60% passing to the particle diameter at 10% passing:

$$U = \frac{d_{60}}{d_{10}} = \frac{5}{0.150} = 33.34$$ **Equation 4.9**

The coefficient of curvature is defined as follows;

$$C = \frac{d^2_{30}}{d_{10} * d_{60}} = \frac{1.18^2}{0.15 * 5} = 1.87$$ **Equation 4.10**

Soil is uniformly graded when U<5 and well-graded when U>5 and C is between 1 and 3. According to the grading analysis of MSWI-BA shown, the uniform coefficient of MSWI-BA was greater than 5, and the coefficient of curvature was between 1 and 3. Therefore, MSWI-BA could be classified as well graded soil.

Materials become frost susceptible when the content of fines reaches a high level for capillary sorption of water to occur. In soils, this level is reached when the percent of fraction under 0.075μm sieve exceed 10% to 15%. The proportion of grains with diameter below 75μm for MSWI-BA did not exceed these limits (**17**), which indicated that MSWI-BA may possess good frost susceptible to be used as fill.

The pH of raw MSWI-BA, which were measured using a liquid to solid ratio (l/s) of 10 varied from 11 to 10 after 300 hours. This range of pH was similar to values reported in elsewhere (**18**, **19**,). Meima et al. (**18**) reported a pH range between 10 and 10.5 for freshly quenched MSWI-BA using a l/s =5 for 24 hours. In general, materials whose pH values are equal or higher to 12.5, are identified as corrosive materials (**20**). However, raw MSWI-BA samples examined did not excess that limit. In addition, the X-ray fluorescence analysis of major and minor elements contained in the MSWI-BA indicated the absence of high concentrations elements, such as Zn, P, Mn, Ba, Cr, As, Cr, Cu and Ni, which can cause a risk to human health and/or the environment.

4.5.2 Properties of MSWI-BA with ∅<212μm

Since this research programme aims to investigate the influence of replacing cement with a fine fraction, the physical and chemical properties of MSWI-BA with ∅<212μm has been compared with cement and cement replacement materials such slag and fly ash. For example, it was observed a significant difference in the particle densities between the fine fraction and cement. That can suggest that the fine fraction had higher volume of internal non-accessible pores than cement.

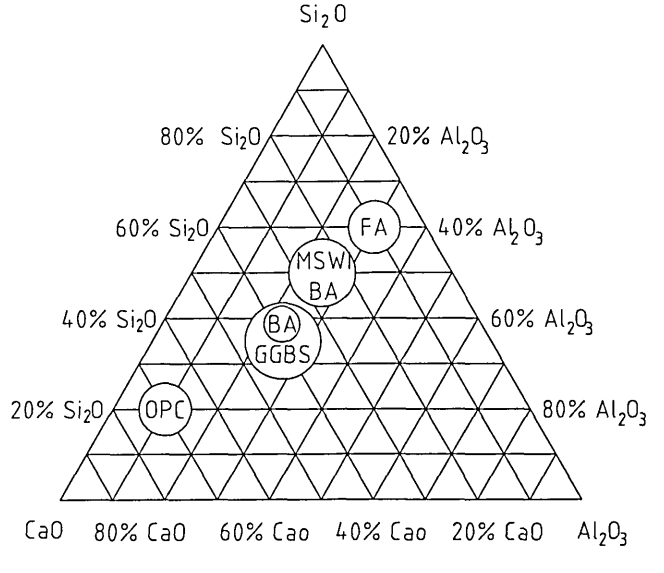
Table 4.10 compares the water content, densities and LOI for the fine fraction of MSWI-BA (∅<212μm) and a "MSWI-BA" with ∅<150μm, fly ash and slag reported elsewhere (**21**,(**22**,**23**). Bulk density for MSWI-BA was lower than the recommended

value for fly ash and for the averaged value reported by Filipponi et al. (**21**). In addition, significant differences in SO_3 and Cl contents have been observed for MSWI-BA compared with fly ash and slag specifications. On the other hand, LOI and water content of MSWI-BA with Ø<212μm were similar to those recommended for fly ash and slag.

Table 4.10. Comparison of Characteristics of MSWI-BA with other waste

	MSWI-BA Ø<212μm	"MSWI-BA" (21) Ø<150μm	FLY ASH (22)	SLAG (23)
water content (%))	<1	N/A	<0.5	<1
Bulk Density (kg/m^3)	604	1140-1425	>2000	N/A
Specific gravity	2.27	2.43-2.46	N/A	N/A
LOI (%)	1.05	2.95-8.47	7-12	<3
SO_3 (%)	9.2	N/A	<2	<2
Cl (%)	1.3	N/A	<0.10	<0.10

Figure 4.7 shows a ternary system which includes percentages of SiO_2, CaO and Al_2O_3 for typical cement (**24**), low-lime fly ash (**25**), slag (**26**), "MSWI-BA" (**21**) and MSWI-BA used throughout this research programme. For MSWI-BA, the oxide percentages of the fraction with Ø<212μm were calculated by averaging values obtained using pressed (method 1) and fused samples (method 2) methods. The percentages of SiO_2, CaO and Al_2O_3 for "MSWI-BA" (**21**) were calculated by averaging three different MSWI bottom ashes whose diameters were less than 150μm.



	SiO_2 (%)	CaO (%)	Al_2O_3 (%)
Cement (24)	17-25	60-67	3-8
Fly Ash (25)	44-56	2-6	17-28
Slag (26)	33-41	33-45	10-16
"MSWI-BA" (21)	40-57	13-20	9-12
MSWI-BA	24-35	23-38	11-14

Figure 4.7. Comparison of SiO_2, CaO and Al_2O_3 contents

SiO_2, CaO and Al_2O_3 contents of MSWI-BA were within the oxide range for slag whereas they were different from the "MSWI-BA" imported by Filopponi et al (**21**). The oxide contents for MSWI-BA were between those of fly ash and slag.

4.5.3 Properties of MSWI-BA with 212μm<∅<2.36mm

The examination of particle density and bulk density suggested that the coarse fraction contained great level of permeable pores and large empty space with particles. The low bulk density for the coarse fraction of MSWI-BA can be due to the heterogeneity of the particles. Irregular shapes and particle size distributions reduces the packing of particles, thereby, increasing their occupied volume. The determination of bulk density using methods A (kerosene) and B gave similar results. The slightly higher values for bulk density using method A were due to a major compaction of particles when the dilatometric liquid is used.

For the coarse fraction of MSWI-BA with 212μm<∅<2.36mm, LOI percentage and contents of chlorides and of sulphur oxide, expressed as SO_3, are 0.3, 5.5 and 1.1 and 0.3 respectively. These values permit to use this fraction of MSWI-BA as aggregates in normal concrete according to BS 882 (**12**). However, these oxides are higher than those specified for lightweight aggregates used in masonry units and structural concrete. In addition, the grading analysis of fraction of MSWI-BA with ∅<2.36mm (see Figure 4.3,) is between the limits for grading class M fine aggregates according to BS 882 (**12**). Chemical composition and pH of MSWI-BA with 212μm<∅<2.36mm, as reported for raw MSWI-BA, do not represent any risk to human health and the environment. In addition, the slight lower pH exhibited for MSWI-BA with 212μm<∅<2.36mm compared with MSWI-BA with ∅<212μm is associated with the lower CaO content in the former MSWI-BA fraction than in MSWI-BA with ∅<212μm.

4.6 CONCLUSIONS

This chapter has examined the properties and chemical properties for four fractions of MSWI-BA; 1) raw fraction (particle diameter (∅) around 10mm); 2) MSWI-BA with ∅<2.36mm (ground); 3) MSWI-BA with ∅<212μm; and 4) MSWI-BA with 212μm<∅<2.36mm. The physical properties included the determination of water content, particle and bulk densities and particle size distribution. The chemical characterisation included the determination of pH, inorganic composition and LOI.

In general, the examination of the physical and chemical properties of MSWI-BA, especially with ∅<2.36mm, revealed initially that this waste can be used as a

construction material. This use will reduce the amount of MSWI-BA sent to landfill sites and the amount of natural materials used.

The properties of the fine fraction of MSWI-BA (∅<212μm) has been compared with cement and well-known admixture materials (i.e. slag and fly ash) with the view to increase the high value of MSWI-BA uses. This comparison indicated that MSWI-BA ∅<212μm exhibited lower particle and bulk density and higher content of unwanted compounds (e.g. Cl and SO_3) than cement. However, the oxides composition of main compounds, which are involved in the formation of calcium silicate hydrates, did not differ significantly from slag and fly ash.

The grading curve of the coarse fraction of MSWI-BA (212μm<∅<2.36mm) indicated that this fraction can be suitable for use as aggregate. However this fraction exhibited lower densities than Class M sand sieved with ∅<2.36mm.

Finally, the examination of chemical composition and pH for raw and the different fractions of MSWI-BA has shown the absence of high concentrations of elements such as Zn, P, Mn, Ba, Cr, As, Cu, which can cause a risk to human health and the environment. Potential environmental and health risks that are associated with the utilisation or disposal of MSWI-BA are evaluated in the next chapter (Chapter 5), where the leaching behaviour of different fraction of un-bound MSWI-BA was examined.

REFERENCES

1 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste Incinerator Residues". Chapter 9; Bottom Ash. Studies in Environmental Science 67. Elsevier 1997

2 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste Incinerator Residues". Chapter 7: Characterisation Methodologies. Studies in Environmental Science 67. Elsevier.. 1997

3 BS EN 1097-5. 1999. Testing for mechanical and physical properties of aggregates. Part 5:Determination of water content by drying in a ventilated oven

4 BS 812 –109. Testing Aggregates. Part 109: Method for determination of moisture content

5 BS 812: Part 2:1999. Testing Aggregates. Method for the determination of density

6 BS EN 1097-3. 1998. Testing for mechanical and physical properties of aggregates. Part 3: Determination of loose bulk density and voids

7 BS EN 1097-7. 1999. Testing for mechanical and physical properties of aggregates. Part 3: Determination of particle density of filler. Pyknometer method

8 BS 812: Part 103:1985. Method for the determination of particle size distribution

9 ASTM D 4980-89. Standard Test method for Screening of the pH in waste

10 BS 3797. 1990. Specification for Lightweight Aggregates for Masonry Units and Structural Concrete.

11 BS EN 196-2. 1995. Methods of Testing Cement. Part 2. Chemical Analysis of Cement

12 BS 882.1992. Specification for Aggregates from Natural Source for Concrete

13 Veabrin. Veabrin Kwaliteitskontrole van AVI-Slakken 87-88. RAP-305/JJS?avd. 1988.

14 Hartlen J. and J. Rogbeck. "Sorted Incinerator Slag used as Fill material". International Conference on Municipal Waste Combustion. Proceeding Vol. 1. Florida, 1989

15 Eighmy T.T., Domingo D., Stampfli D., Krzanowsi J. and J. Eusden D. "The Nature of elements in Combustion residues and their Stabilized Products", pp 541-575. In Proceedings of 1992 Incineration Conference, Albuquerque, New Mexico, 1992

16 Eighmy T.T., Gress D., Zhang X., Tarr S. and Whitehead I. "Bottom Ash Utilisation and Evaluation for the Concord, New Hampshire Waste-to-Energy Facility". Environmental Research Group. Interim Report, UNH Durham, NH 1992

17 Barnes Macmillan G.E. "Soils Mechanics, Principles and Practice. 1995

18 Meima J. and Comans R.N.J. "Geochemical Modeling of Weathering Reactions in Municipal Solid Waste Incinerator Bottom Ash". Environmental Science and Teachnology. Vol, 31, pp1269-1276. 1997

19 Pfrang-Stotz G. and Reichelt J. "Municipal Solid Waste Incinerator Bottom Ash: Characteristics and the Use in Road Construction". Proceedings of International Symposium Use of Incinerator Ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

20 The Great Incinerator Ash Scam. http:it.stlawu.edu?wastenot/316mar95.html

21 Filipponi P., Polettini R., Pomi R. and Sirini P. " Physical and mechanical Properties of Cement-based Products Containing Incineration Bottom Ash". Waste Management. *Article in press.* 2002

22 BS 3892:Part 1:1997. Pulverised-fuel ash. Part 1. Specification for pulverised-fuel ash for use with Portland cement

23 BS 6699. 1992. Specifications for Ground Granulated Blastfurnace Slag for use with Portland cement

24 Neville A. M. " Properties of Concrete". Chapter 1: Portland Cement. Ed. Longman Group Limited, Fourth and Final edition. 1995

25 Lea's ." Chemistry of Cement of Cement and Concrete". Chapter 10: Pozzolan and Pozzolanic Cements. Fourth edition. Ed by Peter C. Hewlett. 1998

26 Lea's ." Chemistry of Cement of Cement and Concrete". Chapter 9: The production of Low-Energy Cements". Fourth edition. Ed by Peter C. Hewlett. 1998

CHAPTER 5: LEACHING BEHAVIOUR OF UNBOUND MSWI-BA

5.1 INTRODUCTION

Much of the concern over either utilisation or disposal of unbound municipal solid waste incineration bottom ash (MSWI-MSWI-BA) is based on the potential contamination of surface and ground water through leaching of metals, sulfates and chlorides (**1**, **2**). Recently, a number of studies have been conducted on the leaching behaviour of unbound MSWI-BA under various conditions. These studies include laboratory and field conditions (**3-5**).

Most of the leaching procedures for unbound MSWI-BA were conducted to simulate either aggressive scenarios or long-term leaching conditions. By varying the physical and chemical parameters of the leaching test and thereby the leaching rate, the aggressive scenario or long-term conditions is simulated (**6**). Physical parameters include leaching duration, type of contact between phases and temperature. Chemical parameters include pH, solubility and occurrence of certain reactions (e.g. re-precipitation).

Moreover, recently published reports on the leaching behaviour of MSWI-BA have focused on the evaluation of geochemical aspects of MSWI-BA (**7-10**). The geochemical assessment requires the examination of leaching behaviour of MSWI-BA under several conditions, in order to predict the minerals that control the release of substances into solutions.

Leaching procedures can be classified into two groups in accordance with Environment Canada 1990 Conference (**11**);

a) Extraction tests: Solid samples are brought into contact with the extractor fluid, known as leachant, under specific conditions without leachant renewal. The resulting leached solutions, known as leachate can be analysed either at the end of the tests or several times during running of the test.

b) Dynamic tests. In these tests, leachant is continuously renewed to maintain a driving force for leaching reaction. Dynamic procedures provide information on the leaching kinetics.

The leaching procedures currently used are based on a combination of the properties of extraction and dynamics tests. The most common leaching tests are;

a) **Batch tests.** These tests are suitable for granular materials where the transfer from solid to liquid phase is optimised by agitation. The existing batch procedures are dependant upon parameters such as number of stages, liquid/solid ratio, type of

extractor fluid, grain size of solid, test duration and type of agitation. Following extraction, leachates are separated from the solid phases. With batch tests, availability tests are widely used as regulatory tests to determine the maximum leaching concentrations of potential toxic compounds in leachates. Table 5.1 provides the recommended experimental parameters for the regulatory batch test that are commonly used. The parameters include the size and mass of solid sample, type of leachant, type of agitation and duration of the test.

Table 5.1. Experimental parameters of most common batch leaching tests

Tested	Sample		Leachant	L/S (L/kg)	Agitation	Duration (hours)
	Size	Mass				
AFNOR (12) X31-210	<4mm	100g	de-mineralised water	10	shaker roller	16
Din 3814-T4 (13)	<10mm	100g	de-ionised water	10	flack inversion	24
ASTM (14)	N/A	350g	de-ionised water	4	shaker	48
CEN TC292 (15)	<4mm	100g	de-mineralised water pH 5-7	10	Gentle agitation	1st step= 24 2nd step=6+8
EPA TCLP Method 1311 (16)	<9.4mm	100g	1. acetic+Na(OH) pH=4.93 1. acetic pH=2.88	20	shaker	18
NEN 7341(17)	N/A	16g	1.de-mineral. pH=7 2.de-mineral. pH=4	50	stirring	1st stage=3 2nd stage=3

b) **Column tests** are suitable for granular and fine materials but they cannot be used for assessing leaching behaviour of cement based systems.

c) **Tank tests** are especially used for monolithic materials (e.g. concrete or mortar specimens). Large solid materials are totally submerged in a tank where the leachant is usually removed several times while the procedure is carried out. For the tank test, the leaching rate depends on parameters similar to the batch tests. Tank tests are discussed in detail in Chapter 8, where leaching behaviour of MSWI-BA contained in cement-based systems is examined.

This chapter examines the leaching behaviour of unbound MSWI-BA. For that purpose, two standard tests; availability test NEN 7341 (**17**) and Toxicity Characteristic Leaching Procedure (EPA TCLP method 1311) (**16**) were used. The comparison of the leachate concentrations obtained from the two procedures may facilitate the identification of mechanisms that may control leaching behaviour of unbound MSWI-BA. The elements

that were considered with special interest for this research programme, were as follows:

a) Major elements (e.g. Ca, Na, K, Si, Al, Mg, Fe) include those elements whose concentrations range between 100-1000mgL^{-1}.

b) Minor elements (e.g. Zn, Pb, Cu, Ba) include those elements whose concentrations range between 0.1-100 mgL^{-1}.

c) Trace elements (Cr, Cd, Ni, Co, Se, As, Sb, Hg) include those elements whose concentrations range between 0.1-100μgL^{-1}.

5.2 EXPERIMENTATION

5.2.1 Materials

Three fractions of MSWI-BA were subjected to leaching testing:

a) Fraction with particle diameter (∅) below 212μm. This fraction was used as a partial replacement of cement in the following chapters.

b) Fraction with 212μm<∅<2.36mm. This fraction was used as a partial replacement of sand.

c) Ground fraction. This fraction consisted of a ground MSWI-BA fraction that was ground by passing the fraction of MSWI-BA with ∅<2.36mm through a hammer mill for 3 minutes. The ground fraction of MSWI-BA was used to identity the influence of grain size on the concentrations of leachates.

In addition, some of the reagents provided in Chapter 3 such as standard solutions for ICP-OES and ICP-MS were employed to conduct metal determinations.

5.2.2 Leaching Procedures

Two leaching procedures were used to study the leaching behaviour of MSWI-BA, EPA TCLP method 1311 and availability NEN 7341 tests. Both tests were carried out on three fractions of MSWI-BA. For each fraction examined, three replicate samples were subjected to each procedure.

In the EPA TCLP method 1311 procedure, two possible leachants (extractor fluid) can be employed as a function of the alkalinity of samples examined. For each fraction of MSWI-BA examined (∅<212μm, 212μm<∅<2.36mm and ground fraction), the selection of appropriate leachant was conducted, as indicated below:

1. The mixture of 96.5 ml of deionised water and 5±0.01 grams of MSWI-BA was agitated using a magnetic stirrer for 5 minutes and the pH recorded.
2. If the pH was above 5, then 3.5ml of HCl 1N were added to the mixture.
3. The mixture of de-ionised water, MSWI-BA and HCl was covered with a watchglass and heated at 50°C for 10 minutes.
4. The solution was left to cool to room temperature.
5. If the final pH recorded was higher than 5, therefore, leachant type 2 is recommended to be used. Leachant 2 consists of a solution of deionised water and acetic acid with a pH=2.88±0.05.

Having found the most appropriate leachant, a mixture formed by 200ml of leachant type 2 and 10±0.01 grams of MSWI-BA samples was agitated approximately at 100rpm for 18 hours. Next, solid and liquid phases (leachate) were separated by vacuum filtration using a 0.45μm glass fibre filter sample.

The availability NEN 7341 procedure consisted of two stages with a duration of three hours for each:

1. *Stage 1*: 800ml of acidified de-ionised water (leachant) were poured on 16±0.01 grams of MSWI-BA. The mixture was agitated using a magnetic stirrer. The pH was kept approximately equal to 7, for 2 and half hours, by adding a few drops of pure HNO_3. Then, the mixture was left to settle for 30 minutes. The solid and liquid phases (leachate) were then separated by vacuum filtration using a 0.45μm glass fibre filter sample.
2. *Stage 2*: Another fresh 800ml volume of acidified de-ionised water was poured into the solid phase keeping the pH approximately equal to 4. Agitation, duration and the filtration for second stage were carried out in a similar way to that of the first stage.

Having finished the NEN 7341 and EPA TCLP method 1311 leaching procedures, leachates from both procedures, were acidified to pH=2 using HNO_3. Acidification was required to avoid precipitation of some metals. Finally, concentrations of elements were analysed using either ICP-OES or ICP-MS techniques or both. Table 5.2 shows the summary of the experimental parameters used for each procedure.

Table 5.2. EPA TCLP method 1311 and NEN 7341 experimental parameter

	TCLP METHOD 1311	NEN 7341
Solid phase mass	10g	16g
leachant (volume)	200ml	800ml
Agitation	Shaking	Magnetic stirrer
Duration	18h	3h for each stage
Extractor fluid (leachant)	Acetic acid (pH=2.88±0.05)	1) pH=7 2) pH=4

5.2.3 Testing

5.2.3.1 Determination of Concentrations using ICP-OES

ICP-OES technique was used to determine the concentrations of Ca, Si, Na, K, Al, Mg, Fe, Ba, Ni, Pb, B, Mn, Cu and Zn. For these elements, concentrations ranged between 1000 and 1 mgL^{-1}.

All leachates of the three fractions of MSWI-BA (∅<212μm, 212μm<∅<2.36mm and ground) were analysed the in same day. Instrumental ICP-MS conditions were optimised using a tuning solution before the analysis was undertaken. More detailed information about ICP-OES testing is provided in Chapter 3.

Table 5.3 shows the dilutions, the standard solutions and the regression coefficient (R^2) for the calibration curves. In addition, for each leaching procedure, the detection limits, expressed in mgL^{-1}, are also shown.

For each element analysed, dilutions of leachates were made considering that the expected concentration of the element was nearly the middle of the calibration curve. For example the Ca concentrations in the leachates ranged from 1500 to 2500 mg L^{-1}. Therefore, the dilutions used were 50 (1500/50=30) and 100 (2500/100=25) and calibration solutions were 0, 10, 25 and 50. Calibration curves were built with at least four concentration points. Standard solutions were prepared from 1000 or 10000 mgL^{-1} ICP-MS certified standards diluting with 1% HNO_3. In order to check reliability of concentration readings, two dilutions were tested for each element. For all elements, correlation coefficient values were close to 1. Detection limits for both leaching procedures (NEN 7431 and TCLP) were calculated using Equation 5.1. The minimum detectable concentration is equal to three times the standard deviation (S_b) obtained from the concentrations of the five blanks (see Chapter 3).

$$\text{detection limit} = 3S_b \qquad \text{Equation 5.1}$$

Table 5.3. Analysis details for the determination of elements using ICP-OES

	Dilution ratio	Standards (mgL^{-1})	R2	Detection limits	
				NEN 7341	TCLP 1311
Ca	50, 100	0, 10, 25, 50	1.0000	0.09	0.02
Si	0, 25	0, 1, 10, 25	0.9952	0.11	0.22
Na	0, 25	0, 1, 10, 25, 50	0.9999	0.01	0.02
K	0, 25	0, 1, 10, 25, 50	1.0000	0.07	0.05
Mg	0, 25	0, 1, 10, 25	1.0000	0.02	0.01
Al	0, 25	0, 1, 10, 25	0.9999	0.03	0.01
Fe	0	0, 1, 10, 25	0.9998	0.01	0.01
Ba	0	0, 1, 5, 10	0.9997	0.01	0.01
Ni	0	0, 1, 5, 10	0.9976	2.09	2.79
Pb	0	0, 1, 5, 10	0.9985	0.22	0.5
B	0	0, 1, 5, 10	1.000	0.03	0.03
Mn	0	0, 1, 5, 10	0.9996	0.02	0.02
Cu	0, 5	0, 1, 10, 25	0.9998	0.02	0.01
Zn	0, 5	0, 1, 10, 25	0.9908	0.05	0.02

5.2.3.2 Determination of Concentrations using ICP-MS

The elements subject to IPC- MS testing were B, Cr, Ni, Mn, Co, Cu, Zn, As, Se, Mo, Cd, Sn, Hg, Ba, and Pb. Prior to analysing the concentrations of these elements, optimisation of ICP-MS testing was conducted. The optimisation of ICP-MS analysis consisted of determining the isotope and method that gave less interference and better sensitivity. Analysis methods include standard addition (SA), external calibration (EC) and internal standard (IS).

- Selection of isotope used throughout ICP-MS testing

Since ICP-MS technique allows isotopic analysis, some isotopes of the same element were tested (See Chapter 3). The choice of isotope examined was based on selecting ones that showed less interference with Ca, K, Na, SO_4^{2-} and Cl^{1-} and high abundance as provided in the CP-MS guide manual (see appendix A).

In order to conduct the isotopic evaluation five standard solution series were prepared. Each series included four standard solutions with concentrations of 0, 1, 5, 25 μgL^{-1} of each element examined. Series 1, represented as S1, was prepared by diluting certificated standard solutions with a solution of 1% HNO_3 (m/m). Series 2 (S2), 3 (S3), 4 (S4), and 5 (S5) were prepared by varying the concentrations of matrix compounds as shown in Table 5.4. Results obtained from calibration series suggested that the most appropriate isotope for each element were B(11), Cr(52), Ni(60), Cu(65), Zn(66), Se(82), Mo(95), Cd(114), Sn(120), MSWI-BA(138), Hg(202) and Pb(208). When isotopes from the same element exhibited similar behaviour, the isotope that presented high sensitivity to small changes in concentration was chosen. These isotopes were chosen for further analysis.

Table 5.4. Calibration solutions for different series

Series ID	Matrix composition
S1	1 % HNO_3
S2	10mgL^{-1} Ca and 5mgL^{-1} Na
S3	50mgL^{-1} Ca, 20mgL^{-1} Na and 25mgL^{-1} K
S4	100mgL^{-1} Ca, 20mgL^{-1} Na, 25mgL^{-1} K
S5	100mgL^{-1} Ca, 20mgL^{-1} Na, 25mgL^{-1} K 40mgL^{-1} SO_4^{2-} and 40mgL^{-1} Cl^{1-}

In addition, a second isotopic analysis was carried out using leached samples. The purpose was to examine if other elements or compounds of the matrix that were not considered in the previous five standards series, could interact differently with the isotopes of the same elements. This second analysis consisted of diluting the leached samples, while the concentrations for elements of interest were kept constant. This was achieved by adding to the sample equal element concentrations to the dilution made. The second isotopic analysis showed that the most appropriate isotopes were the same as the isotopes chosen previously when Ca, K, Na, SO_4^{2-} and Cl^{1-} effects were examined.

- Selection and concentration of the internal standard

Two elements, Sc^{45} and In^{115} were used as internal standards (IS). According to the atomic numbers of elements examined, Sc was selected for the determination of B, Cr, Mn, Co, Ni, and Cu, whereas In was used for Zn, As, Se, Mo, Cd, Sn, Ba, Hg and Pb. For elements, (e.g. Ni, Cu, Zn, As and Se), whose atomic numbers were in the middle of that of Sc and In, both IS were examined. Thus, two standard series were prepared

containing both, Sc or In. Results of this standard series showed that there was not a significant difference between both IS.

An IS concentration of 25 μgL^{-1} was used for all elements throughout the analysis. A unique concentration of isotope was used to reduce the number of dilutions and solution standards to be prepared.

- Standard additions

Some elements (e.g. Co, As, Se, Hg) exhibited concentrations below $5\mu mL^{-1}$. These elements were analysed using standard additions. For this group of elements, concentrations were determined by spiking samples with known concentration. Standard Addition is discussed in detail in Chapter 3.

- Determination of detection limits for element analysis using ICP-MS

The detection limits for each element using ICP-MS were calculated as described in Chapter 3 and section ICP-OES (see section 5.2.3.1).

- Controlling parameters during analysis using ICP-OES and ICP-MS

In order to check for instrumental drift during the measurement a blank and two standard solutions were tested at the beginning of the analysis and after every five samples. If the concentrations of blanks and standard solutions varied by more than 5% compared with the previous reading, a recalibration of the instrument was undertaken.

Because of the concentrations of Na, Ca and other alkalis in the sample matrix deposits were formed in the samples cone resulting reduction in sensitivity. To reduce this contamination, a solution of 5% (v/v) HNO_3 was aspirated into the plasma to clean the sampling cone.

Table 5.5 shows dilutions, standards, type of analysis (e.g. standard addition, external calibration) and internal standards using ICP-MS technique. In addition, detection limits of the elements examined are provided for both leaching procedures used (NEN 7431 and TCPL).

5.2.3.3 Reported Data from ICP-OES and ICP-MS

Net concentrations were calculated by subtracting blank concentrations from the sample concentration readings. Concentrations reported were calculated by averaging the net concentration of three identical samples analysed. Standard deviation (SDEV) and relative standard deviation (RDEV) were calculated as described in Chapter 3.

When the relative standard deviations were higher than 20%, the two identical samples that gave lower RDEV were only considered.

Table 5.5 Analysis details for determination of elements using ICP-MS

Isotopes	Dilution	Standards		Mode	IS[a]	Detection limit	
		µg L^{-1}	Type			NEN 7341	TCLP
B(11)[I]	25, 50	0,1,5,25,50	S1[b]	EC[c]	Sc	1.33	0.14
Cr(52)	25	0,1,5,25,50	S1[b]	EC[c]	Sc	0.12	1.19
	5	0,1,5,25,50	S5[d]	EC[c]			
Mn(55)[II]	25, 50	0,1,5,25,50	S1[b]	EC[c]	Sc	14.73	1.50
Co(59)	5	0,1,5,25,50	S5[d]	EC[c]	Sc	0.12	0.01
	0	0,1,5, 25		SA[e]			
Ni(60)[III]	25	0,1,5,25,50	S1[b]	EC[c]	Sc	17.81	0.23
	5	0,1,5,25,50	S5[d]	EC[c]			
	0	0,1,5, 25		SA[e]			
Cu(63)[IV]	50	0,1,5,25,50	S1[b]	EC[c]	Sc	18.01	13.22
Zn(66)[I]	50	0,1,5,25,50	S1[b]	EC[c]	In	101.01	14.13
As(75)	5	0,1,5,25,50	S5[d]	EC[c]	In	0.02	0.35
	0	0,1,5, 25		SA[e]			
Se(82)	0	0,1,5, 25		SA[e]	In	0.02	0.03
Mo(98)	5	0,1,5,25,50	S5[d]	EC[c]	In	0.13	0.09
	0	0,1,5, 25		SA[e]			
Cd(114)	25	0,1,5,25,50	S1[b]	EC[c]	In	0.42	0.01
	5	0,1,5,25,50	S5[d]	EC[c]			
Sn(120)	0	0,1,5, 25		SA[e]	In	0.25	0.12
Ba (137)[VI]	25, 50	0,1,5,25,50	S1[b]	EC[c]	In	8.16	0.62
Hg(202)	0	0,1,5, 25		SA[e]	In	1.73	0.79
Pb(208)[VII]	50	0,1,5,25,50	S1[b]	EC[c]	In	58.72	2.39

[I,II,II,IV,V,VI,VII] these elements were also analysed using ICP-OES,

[a] Internal standard,

[b] Standard made with 1% HNO_3 (see Table 5.4),

[c] External calibration,

[d] Standard made with Ca, Na, K, SO_4^{2-} and Cl^{1-} (see Table 5.4),

[e] Standard Addition

5.3 RESULTS AND DISCUSSION

5.3.1 Leachate Concentrations for MSWI-BA with Ø<212μm and 212μm<Ø<2.36mm

Table 5.6 provides leachate concentrations of all the elements examined, expressed in milligram of element per kilogram of MSWI-BA, using the leaching procedures TCLP and NEN 7341. Leachate concentrations are reported in decreasing order. Elements with the highest leachate concentrations are at the top of the table (e.g. Ca, Si, Na, K, Al), whereas those with the lowest concentrations (e.g. As, Mo, Se, Sn and Hg) are at the end of the table.

The compositions of leachates for each fraction of MSWI-BA were as follows:

MSWI-BA with Ø<212μm

1. From 100 to 1 gram per kilogram of MSWI-BA, in decrease order: Ca, Na, K, Si, Al, Fe, Mg and Zn.
2. From 0.9 to 0.1 grams per kilogram of MSWI-BA: Pb, Cu, Mn and Ba.
3. From 60 to 10 milligrams per kilogram of MSWI-BA: B, Ni, Cd and Cr.
4. From 7 to 0.1 milligrams per kilogram of MSWI-BA; Co, As, Mo, Se, Sn and Hg.

MSWI-BA with 212μm<Ø<2.36mm

1. From 60 to 1 gram per kilogram of MSWI-BA, in decrease order: Ca, Si, Na, K, Al, Fe, Mg and Zn.
2. From 0.3 to 0.2 grams per kilogram of MSWI-BA: Pb, Cu and Mn.
3. From 80 to 20 milligrams per kilogram of MSWI-BA: Ba, B, Ni and Cd.
4. From 5 to 0.1 milligrams per kilogram of MSWI-BA; Co, As, Mo, Se, Sn and Hg.

Results of TCLP leaching procedure showed that the concentrations of Ca, Na, K, B, Cr, As, Mo, Se and Hg were significantly higher in leachate of MSWI-BA fraction with Ø<212μm than for fraction with 212μm<Ø<2.36mm. In contrast, the leachates of MSWI-BA with 212μm<Ø<2.36mm exhibited higher concentrations of Si, Al, Fe and Zn than for fraction with Ø<212μm. Concentrations of Mg, Pb, Cu, Mn, Ba, Ni, Cd, Co and Sn did not differ substantially between both leachates. Leachates obtained in accordance with NEN 7341 showed slightly different trend to those obtained using TCPL procedure. The concentrations of Ca, Pb, Cu, Ba, Cr and As were significantly higher in leachates of MSWI-BA fraction with Ø<212μm than those for fraction with

212μm<Ø<2.36mm. However, concentrations of Si, Al and Fe were higher in leachates of MSWI-BA fraction with 212μm<Ø<2.36mm than of that for fraction with Ø<212μm. Concentrations of Na, K, Mg, Zn, Mn, B, Ni, Cd, Co, Mo, Se, Sn, Hg did not differ between both MSWI-BA fraction.

Table 5.6. Leachate concentrations, in mg/kg, for MSWI-BA with 212μm<Ø<2.36mm and Ø<212μm using TCLP 1311 and NEN 7341 leaching procedures

	TCLP 1311		NEN 7341	
	212μm<Ø<2.36mm	Ø<212μm	212μm<Ø<2.36mm	Ø<212μm
Ca	15480	33290	56150	96550
Si	1067.80	179.28	13425.00	2828.28
Na	1405.00	2819.00	3814.25	3631.25
K	978.30	1983.00	2521.13	2596.63
Al	308.10	10.43	8996.25	654.78
Fe[a]	62.65	<1	6842.50	588.83
Mg	415.30	437.20	3709.56	2697.13
Zn	78.58	25.68	1538.50	1270.00
Pb	54.92	48.07	278.00	919.00
Cu	15.80	20.89	255.00	679.00
Mn	14.72	15.17	178.94	212.55
Ba	6.34	8.06	83.40	139.43
B	5.97	31.57	50.26	60.52
Ni	1.07	1.00	22.63	23.65
Cd	5.40	6.38	18.59	23.10
Cr	1.05	3.44	5.30	10.95
Co	0.26	0.39	6.06	7.00
As	0.17	0.31	0.54	4.12
Mo	0.56	2.80	2.24	2.18
Se	0.15	0.32	1.04	1.14
Sn	0.04	0.04	0.24	0.23
Hg	0.08	0.36	0.18	0.10

[a] Leachate concentrations of iron were below the detection limit of the ICP-OES for MSWI-BA with Ø<212μm. Hence, they were not reported.

5.3.2 Effect of Leaching Procedure on Leachate Concentrations

5.3.2.1 MSWI-BA with Ø<212μm

Figure 5.1 (a-d) shows total concentrations of leachates that were in accordance with EPA TCLP method 1311 and NEN 7341 leaching procedures. The figure includes four charts that provide concentrations for (a) Ca, Na, K, and Al, (b) Si, Fe, Mg, Cu, Zn and Pb, (c) B, Cr, Mn, Ni, Ba and Cd and (d) Co, As, Se, Sn Hg and Mo. In Figure 5.1-(a-c), the concentrations are expressed in milligram of element per kilogram ($mgkg^{-1}$) of MSWI-BA whereas in Figure 5.1 (d) they are expressed in microgram of element per kilogram (μgkg^{-1}) of MSWI-BA.

In general, concentrations were higher using leaching procedure NEN 7341 than TCPL for most of the elements examined. The higher level of extraction achieved using NEN 7341 can mostly be attributed to the lower pH (pH 7 during first stage and pH 4 for the second stage) used during NEN procedure compared with TCLP. Despite that the initial pH was nearly 3 for TCPL procedure, it increased rapidly to 12 and did not go down to 10.5 during the 18 hours. In addition, the type of agitation employed in NEN 7341 (stirring) may facilitate the solubility of elements compared with the agitation used in EPA TCLP method 1311 (shaking).

Elements such as Al, Si Cu, Zn, Pb, Mn, Ni, Ba, Co, and As exhibited leachate concentrations 10 times bigger using the NEN 7341 procedure than TCLP method 1311. Mo and Hg (see Figure 5.1 (d)) were the only elements that showed higher concentrations using EPA TCLP than NEN 7341. The leachability of these elements was dependent on leaching duration and type of leachant. The leaching duration effect suggested that Mo and Hg may be associated with mineral phases that were accessible only when the other phases had passed into solution. Mo and Hg may be encapsulated and they can not move to solution (leachates) until other elements were already extracted or passed to solution. The type of leachant influence suggested not only that Mo and Hg may be more soluble at neutral pH (i.e pH 7) than a low pH, but also that they may be more soluble in presence of acetic acid (TCLP) than in nitric acid (NEN 7341).

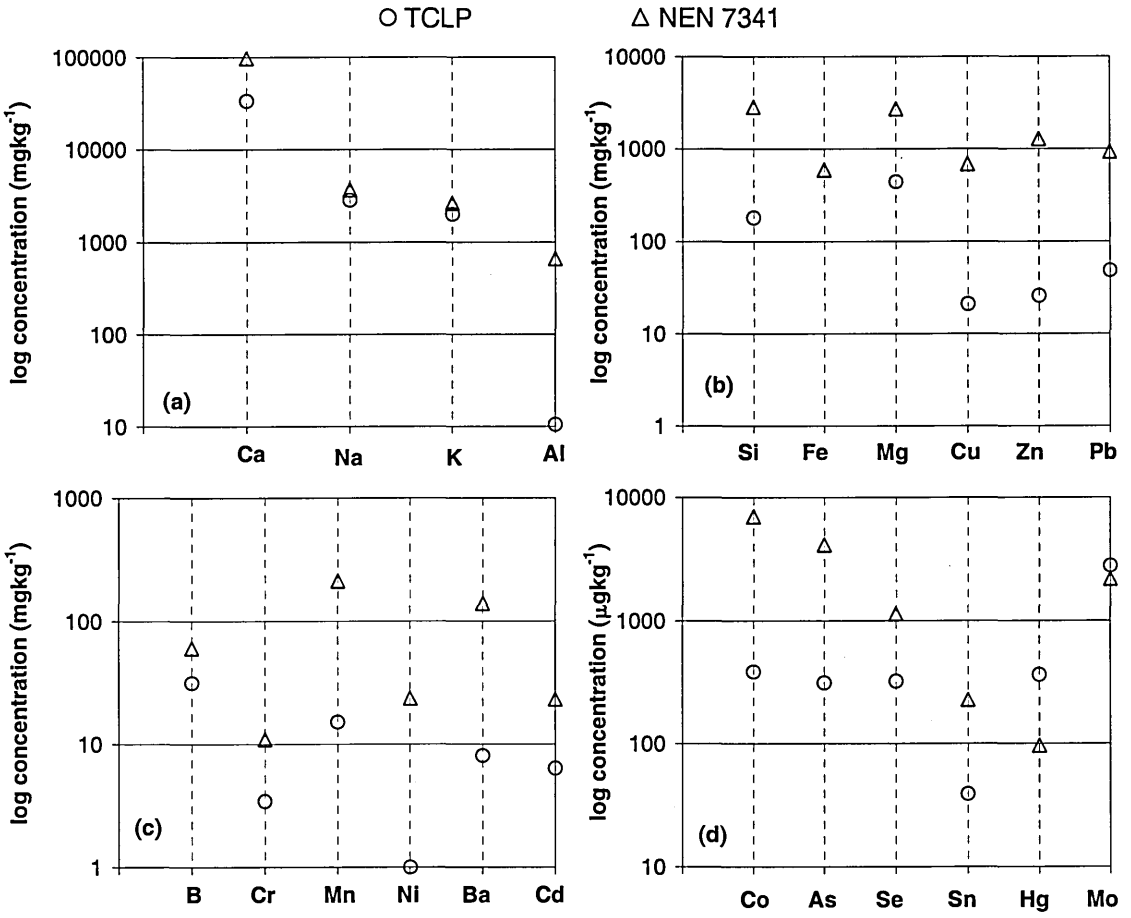


Figure 5.1. Leachate concentrations for MSWI-BA with Ø<212µm using NEN 7431 and TCPL leaching procedures

5.3.2.2 MSWI-BA with 212µm<Ø<2.36mm

Figure 5.2-(a-d) shows leachate concentrations for MSWI-BA fraction 212µm<Ø<2.26mm. Leaching procedure symbol, concentration units and elements in the four charts are the same that those used in Figure 5.1.

For all elements examined, concentrations were higher using leaching procedure NEN 7341 than TCPL. As mentioned in previous section, the difference in concentrations between both leaching procedures may be attributed to the pH, type of leachant and the agitation used for each leaching procedure.

The leachate concentrations of Al, Si, Fe, Cu Zn, B, Mn, Ni, Ba and Co using NEN 7341 procedure were 10 times bigger than those using TCLP. This difference in concentrations between both leaching procedures was not very large for Na, K Pb, Cd, As and Hg concentrations.

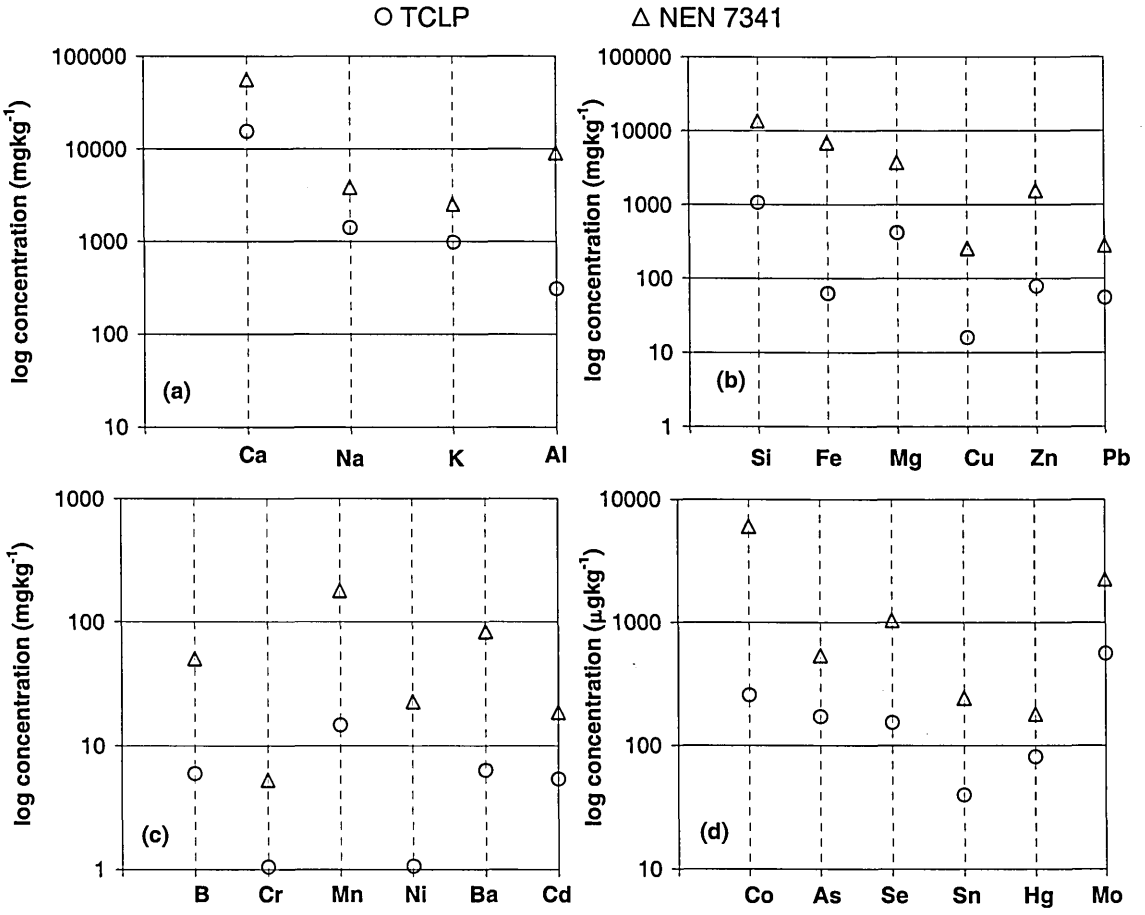


Figure 5.2. Leachate concentrations for MSWI-BA with 212μm<Ø<2.36mm using NEN 7431 and TCPL leaching procedures

5.3.2.3 Comparison between MSWI-BA with Ø<212μm and 212μm<Ø<2.36mm

Figure 5.3 (a-d) shows comparison of concentration ratios for MSWI-BA fraction with Ø<212μm and 212μm<Ø<2.26mm. For each fraction of MSWI-BA, the concentration ratio of each element was calculated dividing the concentrations obtained using leaching procedure NEN 7341 by that using TCLP leaching procedure. The figure includes four charts that show concentration ratios for; (a) Ca, Na, K and Mg; (b) B, Cr, Se, Mo, Sn, Hg and Cd; (c) Si, Mn, As, Ba and Pb and (d) Co, Ni, Cu, Zn and Al.

Figure 5.3 (a-b), shows with the exception of Sn and Cd, that the concentration ratios of Ca, Na, K, Mg, B, Cr, Se, Mo and Hg were higher for MSWI-BA with 212μm<Ø<2.36mm than for fraction with Ø<212μm. This indicated that the increase in leachability as a result of using more acidic leaching procedure (NEN 7341) was higher for MSWI-BA with coarser grains 212μm<Ø<2.36mm than for finer grains Ø<212μm. In other words, the use of a low pH (NEN 7341) facilitate more the extraction of Ca, Na, K, Mg, B, Cr, Se, Mo and Hg in the MSWI-BA with 212μm<Ø<2.36mm than in the MSWI-BA with Ø<212μm. This effect was especially significant for Mg, B, Se and Mo.

However, the need to use lower pH as particle size increases was not observed for Sn and Cd ratios. These ratios were similar for both fractions of MSWI-BA.

Figure 5.3 (c-d) indicate, with the exception of Co ratios, that the concentration ratios of Si, Mn, As, Ba, Pb, Co, Ni, Cu, Zn and Al were higher for MSWI-BA with ∅<212μm than for MSWI-BA with 212μm<∅<2.36mm. This could be attributed to the fact that the low pH used in NEN was not sufficient to completely dissolve some elements (e.g. Mn, As, Ba, Cu and Ni) due to the coarse particle size of MSWI-BA with 212μm<∅<2.36mm, whereas it was effective for MSWI-BA with ∅<212μm. The low pH used in NEN 7341 leaching procedure coupled with the fine particle size of MSWI-BA with ∅<212μm increased significantly the leachability of those elements (i.e. Zn, Pb and Al) that exhibited low leachability using TCLP. The difference in concentration ratios was significantly high for As, Pb, Cu, Zn and Al. These were approximately 8, 12, 14, 30 and 35 points respectively. However, Ni ratios were similar for both MSWI-BA fractions and Co ratios were higher for MSWI-BA with ∅<212μm than for MSWI-BA with 212μm<∅<2.36mm.

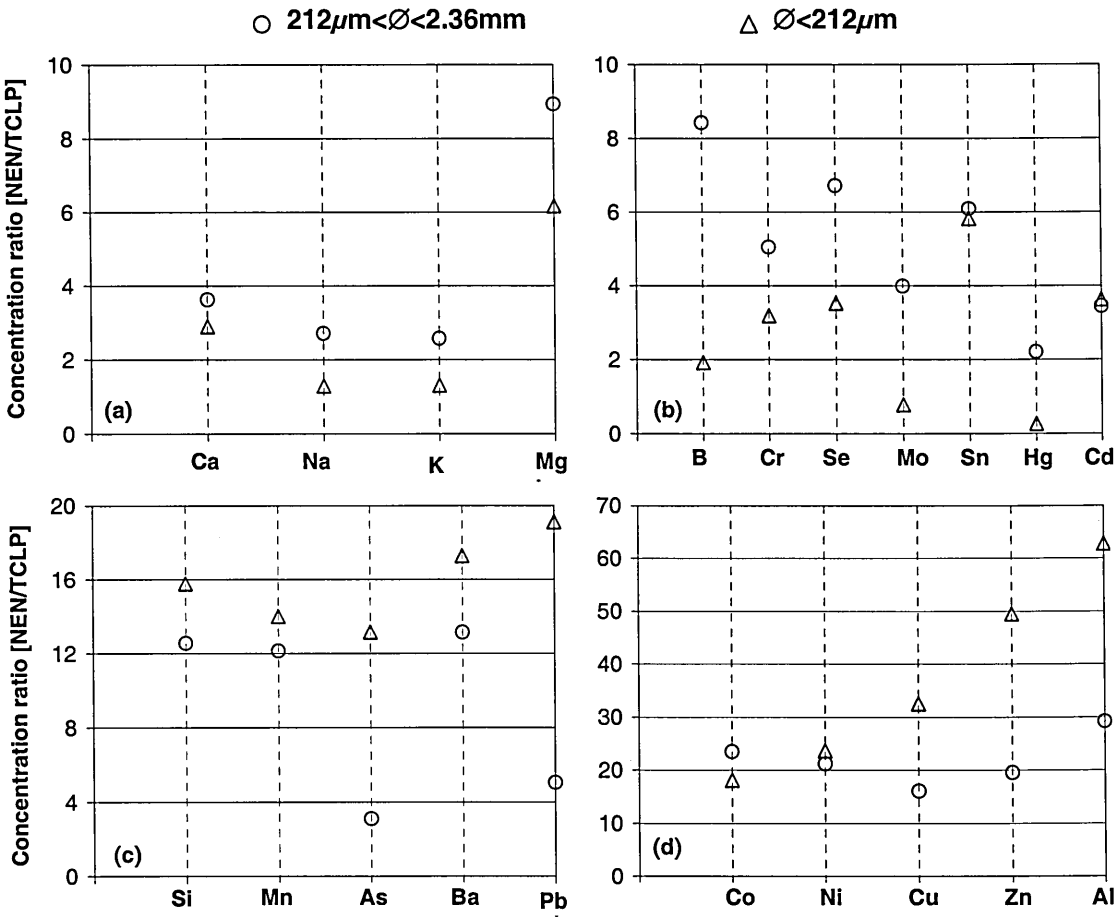


Figure 5.3. Ratio of concentrations using NEN 7341 and TCLP procedures for MSWI-BA with Ø<212μm and 212μm<Ø<2.36mm

5.3.3 Effect of Leachant pH on Leachate Concentrations

5.3.3.1 MSWI-BA with Ø<212μm

Table 5.7 shows the leachate concentrations of Ca, Si, Na, K, Mg, Al, Fe, Mn, Cu, Zn, Ba, and Pb for MSWI-BA with Ø<212μm. Standard deviations between the concentration values of three replicate samples are also reported. Leachates were obtained using the NEN 7341 procedure that had two leaching stages of the same duration (3 hours each); the first stage was carried out using a leachant at pH 7, whereas the second stage was carried out at pH 4. Concentrations of both leachates were compared to evaluate the influence of the leachant pH on leachability.

Concentrations of Si, Mg, Al and Fe were significantly higher in leachates obtained from the second stage (pH 4) than that from first stage (pH 7). This suggested that the leachability of these elements was extremely dependent upon pH of leachant used. On the other hand, the concentration of Ca, Na, K, Cu, Zn and Pb were lower using pH 4 than using pH 7. That can be attributed to the solubility of these elements at neutral pH

(pH 7). Mn and Ba showed a slight increase in concentration at pH 4 compared with that at pH 7.

Table 5.7. Concentrations of leachates, expressed in mgL^{-1}, for the first (pH 7) and second (pH 4) extraction stages using NEN 7341 on the MSWI-BA with Ø<212μm

	Ca	Si	Na	K	Mg	Al	Fe	Mn	Cu	Zn	Ba	Pb
Stage 1	1310	2.0	57.8	41.9	12.0	1.2	<1[a]	0.9	10.0	29.1	0.3	12.6
(pH 7)	±14	±1	±1	±1	±1	±0.3	-	±0.1	±1	±5	±0.1	±2
Stage 2	621.0	54.6	14.9	10.1	41.9	11.9	11.7	2.6	3.7	4.0	1.4	5.6
(pH 4)	±2	±7	±1	±1	±1	±3	±2	±0.1	±1	±1	±0.1	±1

[a] Leachate concentrations of iron were below the detention limit of the ICP-OES for MSWI-BA with Ø<212μm. Hence, they were not reported.

Table 5.8 shows the leachate concentrations of B, Cr, Co, Ni, As, Se, Mo, Cd, Sn, and Hg, expressed in μgL^{-1}, for MSWI-BA with Ø<212μm. The table indicates that concentrations of B, Cr, As, Se, Mo, Cd and Sn were substantially higher at pH 7 than at pH 4, whereas Sn and Hg exhibited a slight difference in concentrations for both leachates. The concentration of Ni was approximately 11% higher at pH 7 than at pH 4. However, Co seemed to be extremely dependent upon the leachant pH, being much lower at pH 7 than pH 4.

Table 5.8. Concentrations of leachates, expressed in μgL^{-1}, for the first (pH7) and second (pH 4) extraction stages using NEN 7341 on the MSWI-BA with Ø<212μm

	B(11)	Cr(52)	Co(59)	Ni(60)	As(75)	Se(82)	Mo(98)	Cd(114)	Sn(120)	Hg(202)
Stage 1 (pH 7)	718.6	189.8	18.4	252.2	58.7	14.1	30.1	325.3	2.1	≤1
Stage 2 (pH 4)	491.9	29.2	121.6	220.8	23.7	8.7	13.6	136.9	2.4	≤1

5.3.3.2 MSWI-BA with 212μm<Ø<2.36mm

Table 5.9 shows the leachate concentrations of Ca, Si, Na, K, Mg, Al, Fe, Mn, Cu, Zn, Ba, and Pb for MSWI-BA fraction with 212μm<Ø<2.36mm. Leachates were obtained using the NEN 7341 procedure. Leachate for the first stage (pH 7) showed higher concentrations of Ca, Si, Na, K, Mg, Al, Fe than the leachate for the second stage (pH 4). However, the former leachates (pH 7) exhibited lower concentrations of Cu, Zn and Pb than the latter leachates (pH 4). This difference in leachate concentrations of Cu, Zn

and Pb can be explained by two facts; 1) Cu, Zn and Pb need a pH of 4 to be extracted and 2) these elements were extracted after certain major elements (e.g. Si, Al, and Fe) passed into solution during the first stage (pH 7). The concentrations of Mn and Ba did not differ significantly between leachates obtained at pH 7 and pH 4.

Table 5.9. Concentrations of leachates, expressed in mgL^{-1}, for the first (pH 7) and second (pH 4) extraction stages using NEN 7341 on the MSWI-BA with 212μm<Ø<2.36

	Ca	Si	Na	K	Mg	Al	Fe	Mn	Cu	Zn	Ba	Pb
Stage 1 (pH 7)	961.3 ±17	189.2 ±1	55.0 ±2	36.8 ±1	55.1 ±1	117.1 ±8	78.2 ±20	2.9 ±1	0.6 ±0.1	1.0 ±0.1	1.0 ±0.2	0.4 ±0.1
Stage 2 (pH 4)	161.8 ±21	79.3 ±8	21.3 ±3	13.6 ±2	19.1 ±1	62.8 ±4	58.7 ±5	1.2 ±0.1	4.8 ±1	23.9 ±1	1.8 ±0.2	5.9 ±1.5

Table 5.10 shows the leachate concentrations of B, Cr, Co, Ni, As, Se, Mo, Cd, Sn, and Hg for MSWI-BA with 212μm<Ø<2.36mm. The concentrations of B and Mo were higher at pH 7 than at pH 4, whereas Cr, As and Se concentration were lower compared with that at pH 4. The significantly high concentrations of Co, Ni and Cd at pH 4 indicated that these elements seemed to be extremely dependent upon the pH of the leachant. The concentrations of Sn and Hg did not differ significantly between leachates obtained at pH 7 and pH 4.

Table 5.10. Concentrations of leachates, expressed , in μgL^{-1}, for the first (pH 7) and second (pH 4) extraction stages using NEN 7341 on the MSWI-BA with 212μm<Ø<2.36

	B(11)	Cr(52)	Co(59)	Ni(60)	As(75)	Se(82)	Mo(98)	Cd(114)	Sn(120)	Hg(202)
Stage 1 (pH 7)	577.5	40.8	11.0	27.5	4.5	9.3	40.6	77.1	2.2	≤2
Stage 2 (pH 4)	427.6	65.3	110.1	425.0	6.3	11.6	4.2	294.7	2.7	≤1

5.3.3.3 Comparison between MSWI-BA with Ø<212μm and 212μm<Ø<2.36mm

Table 5.11 and Table 5.12 show the pH of leachant that gave high concentrations for different elements examined for each fraction of MSWI-BA examined.

Table 5.11. Leachant pH that gives high concentrations of Ca, Si, Na, K, Mg, Al, Fe, Mn, Cu, Zn, Ba and Pb in leachates

MSWI-BA fraction	Ca	Si	Na	K	Mg	Al	Fe	Mn	Cu	Zn	Ba	Pb
Ø<212μm	7	4	7	7	4	4	4	4	7	7	4	7
212μm<Ø<2.36mm	7	7	7	7	7	7	7	7	4	4	4	4

Table 5.12. Leachant pH that gives high concentrations of B, Cr, Ni, As, Se, Mo, Cd, Sn and Hg in leachates

MSWI-BA fraction	B	Cr	Co	Ni	As	Se	Mo	Cd	Sn	Hg
Ø<212μm	7	7	4	7	7	7	7	7	4	7,4
212μm<Ø<2.36mm	7	4	4	4	4	4	7	4	4	7,4

Table 5.11 shows that the concentrations of Ca, Na, K and Ba were the highest at the same pH for both MSWI-BA fractions. For both fractions, Ca, Na and K exhibited higher concentrations at pH 7 than at pH 4, whereas Ba showed higher concentrations at pH 4 than at pH 7. In contrast, the concentrations of Si, Fe, Al, Mn, Cu, Zn and Pb were dependent on the MSWI-BA fraction examined. Si, Mg, Fe, Al and Mn concentrations were higher at pH 4 than at pH 7 for MSW-BA with Ø<212μm, whereas they were higher at pH 7 than at pH 4 for MSWI-BA with 212μm<Ø<2.36mm.

MSWI-BA with 212μm<Ø<2.36mm possessed significantly higher concentrations of Si, Fe and Al and lower concentration of Ca than MSW-BA with Ø<212μm, as shown in Table 5.6. In addition, Ca was expected to be located on the external surface layer of MSWI-BA grains hiding inner elements, as discussed in Chapter 4. Therefore, the reduction in the amount of Ca in MSWI-BA with 212μm<Ø<2.36mm, may facilitate the dilution of Si, Mg, Al, Mn and Fe even at neutral pH, for the fraction with 212μm<Ø<2.36mm. However, for MSWI-BA Ø<212μm with these elements passed to solution when the Ca had already passed.

The discrepancy between both fractions of MSWI-BA about the concentrations of Cu, Zn and Pb was attributed to the higher increase in leachability at pH 4 of the fraction with 212μm<Ø<2.36mm compared with the fraction with Ø<212μm. These elements

could be leached out after major matrix elements (i.e. Si, Al, Fe) had partially moved into solution for the fraction with 212μm<∅<2.36mm.

Table 5.12 shows that the concentrations of B, Co, Mo, Sn and Hg showed similar trend for both MSWI-BA fractions. However, concentrations of Cr, Ni, As, Se and Cd were dependent on MSWI-BA fraction examined. Concentrations of Cr, Ni, As, Se and Cd were higher at pH 4 than at pH 7 for the fraction with 212μm<∅<2.36mm and lower at pH 4 than at pH 7 for the fraction with ∅<212μm. This suggested that these elements passed to solution after leaching of major elements did for fraction with 212μm<∅<2.36mm, whilst due to the fine particle size of MSWI-BA with ∅<212μm they were leached out in the first leaching stage.

In general, the distinct pH behaviour of elements in both fractions of MSWI-BA can be attributed to the differences in particle sizes, element contents and mineralogical compositions between both fractions.

5.3.4 Effect of Particle Size on Leachates Concentrations

In order to compare the effect of particle size on leaching, the MSWI-BA fractions with ∅<212 μm and 212μm<∅<2.36mm were ground to reach a particle size below 75μm. The ground MSWI-BA fractions were subjected to NEN 7341 and EPA TCLP method 1311 leaching procedures. Table 5.13 provides the increase in leachability, in %, as a result of grinding MSWI-BA fractions. Columns 2 and 3 show the increase in extraction with respect to the fraction with ∅<212μm for both leaching procedures and 4th and 5th columns show that for the MSWI-BA with 212μm<∅<2.36mm.

Generally, there was a significant increase in leaching as a result of grinding. This was in agreement with the results reported in previous sections about the influence of particle size on leachability of un-ground fractions. For example, Mg, Mn, Zn, Cr, Ni, Se and Sn exhibited an increase in leachability above 50% for both fractions and both leaching procedures. In addition, it was observed that half of elements (e.g. Ca, Si, Na, K, Mg, Mn, Cu, Zn, Cr, Ni and Sn) exhibited higher extraction levels for TCLP method 1311 than NEN 7341 for both MSWI-BA fractions.

Moreover, grinding facilitated the leachability of the elements that were in the inner phase of the grain of ash. For example, the content of Si for leachates of fraction with 212μm<∅<2.36mm was higher than that for fraction with ∅<212μm. However, as a result of grinding, the increase in leachability of Si for fraction with ∅<212μm was much higher than that for MSWI-BA with 212μm<∅<2.36mm.

Table 5.13. Increase in leachability, expressed as %, as results of grinding the fraction of MSWI-BA with Ø<212μm and 212μm<Ø<2.36mm.

	un-ground/ground concentration ratio for MSWI-BA with			
	Ø<212μm		212μm<Ø<2.36mm	
	NEN 7341	TCPL	NEN 7341	TCPL
Ca	30.6	35.2	59.6	69.9
Si	85.4	94.6	37.1	67.9
Na	24.4	40.4	20.5	70.3
K	32.4	38.4	34.4	69.6
Mg	63.7	52.0	50.1	54.4
Al	96.0	96.7	45.4	3.9
Mn	53.3	71.5	60.6	72.3
Cu	11.8	62.2	66.9	70.6
Zn	50.4	90.7	59.0	71.4
Ba	20.7	31.8	52.5	46.4
Pb	9.9	55.1	72.7	48.7
B(11)	27.8	12.7	40.0	83.5
Cr(52)	72.8	49.9	86.8	84.7
Co(59)	22.0	82.3	21.5	88.1
Ni(60)	73.3	96.7	74.5	96.0
As(75)	27.3	17.9	90.5	45.0
Se(82)	51.3	46.5	55.5	75.8
Mo(98)	56.6	5.5	55.4	81.1
Cd(114)	14.3	15.9	31.0	0.6
Sn(120)	58.2	63.6	55.1	62.7

5.3.5 Maximum Leached Concentrations

The concentrations of all elements increased significantly in the ground MSWI-BA fraction with respect to the un-ground fractions, therefore, concentrations of the ground fractions were considered as the maximum quantity of each element that can be leached.

Table 5.14 provides a comparison of the concentrations in the leachates obtained from TCLP 1311 and NEN 7341 procedures for the ground MSWI-BA fraction and various

regulatory limits. Some of the limits reported are used for assessing the quality of soil and contaminated land in the Netherlands (**18**) and the United Kingdom (**19**) and other values reported are technical concentrations recommended for the use of mineral waste and soils in Germany and the European Union (**20**). All concentrations are expressed in milligram of element per kg of either dried MSWI-BA or soil. In columns 4 and 5, the low values correspond to good quality of soils or land, whereas the upper limits indicate poor environmental quality.

Table 5.14. Comparison of the ground MSWI-BA fraction leachability with limits for soils, contaminated land and mineral waste in the Netherlands (18), the United Kingdom (19), Germany (20) and European Union (20)

	Concentrations expressed in $mgkg^{-1}$ of dried material					
	Ground MSWI-BA		The Netherlands	United Kingdom	Germany	European Union
	TCLP	NEN 7341				
Cr	6.9	40.2	100-800	N/A	100	100
Co	2.2	9.0	20-300	N/A	N/A	N/A
Ni	26.9	88.7	50-500	70	100	50
Cu	53.8	769.9	50-500	130	100	100
Zn	275.1	3100.0	200-3000	300	N/A	N/A
As	0.3	5.7	20-50	10-40	30	10
Se	0.6	2.3	N/A	3-6	N/A	N/A
Mo	3.0	5.0	10-200	N/A	N/A	N/A
Cd	6.4	27.0	1-20	3-15	1	1
Ba	11.8	175.7	200-2000	N/A	N/A	N/A
Hg	0.1	0.1	0.5-10	1-20	N/A	N/A
Pb	107.0	1020.0	50-600	500-2000	200	100

It was observed that the release of Cr, Co, As, Se, Mo, Ba and Hg in the MSWI leachates did not exceed any of recommended limits given for the various countries. However, the concentrations of Ni, Cu, Zn, Cd and Pb exceeded some of those limits. The concentration of Ni using NEN 7341 procedure was higher than the values given in the UK and European Union. The concentrations of Cu and Cd using the same procedure exceeded all limits reported in columns 4-7. Concentration of Zn exceeded Dutch and English values. Pb concentrations exceeded Dutch, German and European limits.

Table 5.15 shows the leachate concentrations of some elements obtained in accordance with the TCLP leaching procedure for the ground MSWI-BA fraction and the tolerable limits for non-hazardous waste in USA. In general, the concentrations of elements reported were below permitted limits except the concentration of Pb that was slightly higher than the imposed limit.

Table 5.15. Comparison of TCLP concentrations of the ground fraction with USA regulatory limits

	Concentrations expressed in mgL^{-1}						
	As	**Ba**	**Cd**	**Cr**	**Pb**	**Hg**	**Se**
limits (USA)	5.00	100.00	1.00	5.00	5.00	0.20	5.00
TCPL	0.02	0.60	0.30	0.30	5.35	0.01	0.02

5.3.6 Comparison Between Chemistry and Leaching Behaviour

Table 5.16 shows the contents of Ca, Si, Al, Fe, Mg, K and Na for the fractions of MSWI-BA with Ø<212μm and with 212μm<Ø<2.36mm and the concentrations of these elements in leachates from the same fractions of MSWI-BA. Contents of Ca, Si, Al, Fe, Mg, K and Na were determined using XRF with fused samples preparation (see Chapters 4 for more details on chemical composition testing). Leachates of both fractions of MSWI-BA were obtained in accordance to NEN 7341 leaching procedure.

Table 5.16. Comparison between chemical compositions and leaching behaviour for fractions of MSWI-BA with Ø<212μm and 212μm<Ø<2.36mm

Elem.	Contents (g/kg of MSWI-BA)		Leachate concentration (g/kg of MSWI-BA)		Extraction (%)	
	Ø<212	**212<Ø<2.36**	**Ø<212**	**212<Ø<2.36**	**Ø<212**	**212<Ø<2.36**
Ca	190.00	107.50	96.55	56.15	50.82	52.23
Si	224.00	316.91	2.83	13.43	1.26	4.24
Al	75.46	81.69	0.65	9.00	0.86	11.02
Fe	38.22	91.56	0.59	6.84	1.54	7.47
Na	21.65	36.53	3.63	3.81	16.77	10.43
Mg	17.25	17.25	2.70	3.71	15.65	21.51
K	15.42	17.23	2.60	2.52	16.86	14.62

Extraction percentages of Ca (50.82% and 52.23%) were the highest within all elements examined for both fractions of MSWI-BA. This was attributed to the high solubility of calcium compounds (i.e. $Ca(OH)_2$, $CaCO_3$, CaO and $CaAl_2O_4$) in water and diluted acid (**21**). The remaining Ca might be in other forms that could not be extracted such as calcium metasilicate ($CaSO_3$), which is insoluble in H_2O or diluted acid (**22**).

Extraction percentages of Si were very poor for both fractions of MSWI-BA despite the great proportion of Si in both fractions examined. This was expected due to the low solubility of silicates, which are not soluble in either H_2O or common acids.

Extractions percentages of Fe, Mg and especially Al were higher for MSWI-BA fraction with 212μm<∅<2.36mm than that for MSWI-BA fraction with ∅<212μm, despite the coarser particle of the former fraction. This suggested that these elements were bonded differently in each fraction examined. For example, in fraction with 212μm<∅<2.36mm, Al might be as $Al(OH)_3$ that is slightly soluble in acid whereas in fraction with ∅<212μm it might be as aluminium silicate that is insoluble in acid, H_2O and alkali (**21,22**). Extraction percentage of Na and K were higher for the fraction of MSWI-BA with ∅<212μm than for fraction with 212μm<∅<2.36mm. This can be attributed to the difference in particle size distributions and chemical bonds between both fractions examined.

5.4 CONCLUSIONS

This chapter has examined the leaching behaviour of unbound MSWI-BA fractions with particle diameters of ∅<212μm and 212μm<∅<2.36mm. Leaching behaviour of these fractions of MSWI-BA has been examined by determining the concentrations of leachates obtained in accordance with NEN 7341 and TCLP leaching procedures.

Conclusions are draw from findings of the examination of leachability and are presented in the following items:

1. Composition of leachates for fractions of MSWI-BA with ∅<212μm and 212μm<∅<2.36mm.
2. Comparison of leachate compositions between both fractions of MSWI-BA examined.
3. Influence of leaching procedure, leachant pH and particle diameter on leachability of MSWI-BA fractions.
4. Potential environmental risk of MSWI-BA due to the release of hazardous elements.

Leachates for both fractions of MSWI-BA examined contained Ca, Si, Na, K, Al, Fe, Mg and Zn as major elements, with concentration ranging from 100 to 1 gram per kilogram of MSWI-BA, followed by Pb, Cu, Mn and Ba with concentration ranging from 0.9 to 0.1 g/kg of MSWI-BA and B. Ni, Cd, Co, Cr, Mo, Se, As, Sn and Hg with concentrations ranging from 60 to 0.1mg/Kg of MSWI-BA. The content of all these elements in leachates was not only dependent upon MSWI-BA examined, but also upon leaching procedures carried out.

For both leaching procedures, the fine fraction of MSWI-BA (∅<212μm) exhibited higher leachate concentrations of Ca, Cr, and As than the coarse fraction (212μm<∅<2.36mm), whereas the coarse fraction gave higher concentrations for Si, Al and Fe. Concentrations of Mg, Mn, Ni, Cd, Co, Sn and Mo did not differ substantially between leachates of both MSWI-BA fractions regardless of leaching procedure. However, concentration of Na, K, Zn, Cu, Ba, B, Se and Hg were either higher or lower in one fraction of MSWI-BA or the other, depending on leaching procedure carried out.

The comparison of leachate concentrations using ether NEN 7341 or TCLP procedure showed that NEN 7341 leachates exhibited higher concentrations than TCLP leachates for most elements. This trend was observed in both fractions of MSWI-BA examined. In particular, the differences in concentrations between both leaching procedures were significant high for Si, Fe, Mn, Ba, Pb, Co, Ni, Cu, Zn and Al. Hence, the leachability of MSWI-BA was increased largely using nitric acid to control the leachant pH below 7 and 4 and stirring agitation (NEN 7341) in comparison with using acetic acid to achieve low initial leachant pH, test pH of 10 approximately and shaking agitation. This suggested that elements examined dissolved as cationic forms that are more soluble in acid conditions and strongly pH dependent than metal in oxanion forms (**5,8**).

Examination of the leachate concentrations obtained individually at pH 7 and pH 4 (first and second stages of the NEN 7341 leaching procedure) showed that the degree of solubility of Si, Mg, Al, Fe, Mn, Cu, Zn Pb Cr, Ni, As, Se, Cd either at pH 7 or 4 was dependent upon the fraction of MSWI-B examined. This discrepancy of pH-solubility effect as a function of MSWI-BA examined was attributed to the difference in particle size, element contents and phases associated to these elements between the both fractions of MSWI-BA. In contract, Ca, Na, K, Ba, B, Co, Mo, Sn and Hg exhibited similar pH- solubility influence regardless of MSWI-BA fraction examined. Ca, Na, K, B and Mo concentrations results higher at pH 7 than at pH 4, whereas Ba, Co and Sn concentration were higher in leachates obtained in stage pH 4.

Grinding fractions of MSWI-BA with ∅<212μm and 212μm<∅<2.36mm to the same particle size increased likewise the leachability of both fractions regardless of the

leaching procedure used. However, grinding these fractions of MSWI-BA did not reduce the difference in the leachate concentrations obtained in accordance to either NEN 7341 or TCLP.

Finally, leachate concentrations of Ni, Cu, Zn, Cd and Pb obtained by leaching the ground fraction of MSWI-BA with ∅<2.36mm exceeded slightly the tolerable limits for soils or mineral waste used within European Union (**18-20**). This suggested that a remediation technique (e.g. stabilisation with cementitious materials) may be required when MSWI-BA is dumped in landfill sites, in order to increase the environmental acceptance of MSWI-BA. However, leachates obtained in accordance with the TCLP procedure for the same fraction of MSWI-BA did not exceed USA regulatory limits.

The next chapter, Chapter 6, will evaluate the performance of mortars containing different fractions of MSWI-BA as a partial replacement of cement and/or sand in order to enhance its utilisation. The use of MSWI-BA in concrete manufacture will not only reduce the amount this waste sent to landfill sites but also the environmental risk due to the well-known capacity of cement-based systems to bind toxic elements or compounds.

5.5 REFERENCES

1 Chandler A.J., Eightmy T.T., Hartlen J., Hjelmar O., Kosson D.S., Sawel S.E., Van der Sloot H.A. and Vehlow J. The International Ash Working Group. "Municipal Solid Waste Incinerator Residues". Physical Aspect of Leaching. Studies in Environmental Science 67. Elsevier Chapter 12: 1997

2 Bodénan F., Azaroual M. and Piantone P. "Forescasting the long-term behaviour of Municipal Solid Waste Incineration Bottom Ash: Rapid Combined tests". Waste Materials in Construction. Ed. Woolley, G.R., Goumans. J.J. J. M. and Wainwright, P.J. Elsevier Science 2000

3 Fällman A. M. "Significance in the Results of Total Composition and Potential Leachability of Screened MSWI MSWI-BA from Different Plants and Sampling Periods". Waste Materials in Construction. Ed. Woolley, G.R., Goumans. J.J. J. M. and Wainwright, P.J. Elsevier Science 2000

4 Meima J.A., van der Weijden R.D., Eighmy T.T. and Comans R.N.J. "Carbonation Process in Municipal Solid Incinerator Bottom ash and their Effect on the Leaching of Copper and Molybdenum". Applied Geochemistry article in press. 2001

5 Johnson C.A. "A Geochemical Perspective on the Factors that Control Long-Term Emission from Municipal Solid Waste Incinerator". Proceedings of International Symposium "Use of Incinerator ash". Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

6 De Groot G.J., Hohberg I., Lamers F.J., Van Der Veen A.M.H., Wassing W.and Quevauviller PH. "Development of Leaching Method for the Determination of Environmental Quality of Concrete". European Commission. BCR Information. 1997

7 Meima J.A. and Commans R.N.J. "Geochemical Modelling of Weathering Reactions in Municiapl Solid Waste Incineration Bottom Ash". Environmental Science Technology No 31 pp 1269-1276. 1997

8 Johnson C.A., Kersten M., Ziegler F. and Moor C. "Leaching Behaviour and Solubility Controlling Solid Phases of Heavy Metal in Municipal Solid Waste Incinerator Ash". Waste Management. Vol.16, Nos. 1-3 , pp 129-134.1996

9 Meima J.A. and Commans R.N.J. "The Leaching of Trace Elements from MSWI Bottom Ash at Different Stages of Weathering". Applied Geochemistry No 14 pp 159-171. 1999

10 Commans R.N.J., Meima J.A. and Geelhoed P.A. "Reduction of Contaminant leaching from MSWI Bottom Ash by Addition of Sorbing Components". Waste Management No 20, pp 125-133. 2000

11 Lewis K., Bradshaw K., Blakey N.C., Turrel J., Henning S.M. and Flavin R.J. "Leaching Tests for Assessment of Contaminated Land. Interim NRA Guidance". National Rivers Authority. 1993

12 AFNOR X31-210.DéChets: Essai de Lixiviation. 1988

13 DIN 3814-T4. German test Deutsche Einheitsverfahren zur Wasser. Abwasser und Schulammum-tersuchung: Schalmm und Sedimente (Gruppe S)

14 American Society for testing Materials: Annual Book ASTM Standard. Part 3. 1997

15 CEN TC 292 WI3: Characterisation of Waste-Leaching-Compliance Test for Leaching of Granular Materials-Determination of the Leaching of Constituents from Granular Waste Materials and sludges. 1996

16 EPA. Toxicity Characteristic Leaching Procedure (TCLP) Method 1311. July 1992

17 NEN 7341 02.95: "Leaching Characteristics of Solid Earthy and Stony Building and Waste materials. Leaching Test. Determination of the leaching availability of Inorganic Compounds

18 Original Dutch Limits for Solis when Assessing Contaminated Land. 1994.

19 Kelly Tables. Trigger Values for Contaminated Soils. 1978

20 European Commission. Directorate General for Environment. WRc Ref: CO4953-2/11768-1. July 2001

21 Handbook of Physicochemical Properties of Elements. Ed Samsonov G.V. 1968

22 Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemical. Donald Mackay, Wan-Ying Shiu, Kuo-Ching. Lewis Published 1995

CHAPTER 6: PHYSICAL AND MECHANICAL PROPERTIES OF MORTAR CONTAINING MSWI-BA

6.1 INTRODUCTION

The use of replacing primary materials (e.g. cement aggregates) with waste is being encouraged and extensively used over the world (**1-7**). Wastes can be used as either cement replacement (e.g. fly ash and slag) or as natural aggregate replacement (e.g. recycled bricks and concrete).

In general, the compressive strength at 28 days and the ratio of strength development with time are commonly used as indicators of the quality of the cement-based materials with or without containing waste (**8**). Despite the fact that compressive strength is one of the most valuable properties of paste, mortar and concrete; it is not normally the only property examined. Other properties including shrinkage and porosity need to be evaluated to assess long-term performance.

Many factors influence the physical and mechanical properties of cement-based systems. These include water to cement ratio (w/c), cement, content and type of aggregates, chemical composition and fineness of binder constituents and level of admixtures replacement. Chapter 2 presents a revision of current knowledge on the chemical, physical and mechanical properties of cement-based systems containing blended materials and recycled aggregates.

In this chapter, the influence of MSWI-BA on the physical and mechanical properties of mortars containing MSWI-BA either to replace the cement and/or sand has been investigated. The properties examined are compressive strength, saturated density, drying shrinkage, porosity, and flexural strength.

6.2 EXPERIMENTATION

6.2.1 Materials

The materials that were used in this chapter were a standard Ordinary Portland Cement which conformed to BS12: 1996 (**9**), class M sand which conformed to BS 882:1992 (**10**), silica sand (90% silicate content) and different fractions of MSWI-BA. The chemical and physical properties of these materials are given in detail in Chapter 3 and Chapter 4.

6.2.2 Mix Proportion

The proportion of binder to aggregate (b:a) was 1:3 and water/binder (w/b) ratio was 0.50 for the majority of mixes. For selected mixes, the w/b ratio was 0.6.

Binders included the standard 42.5N cement and fractions of MSWI-BA (Ø<150μm, Ø<212μm, Ø<300, Ø<600μm and Ø<1.18mm). Cement was replaced with different

levels of these fine fractions of MSWI-BA. Aggregates consisted of class M sand and coarse fractions of MSWI-BA (212μm<∅<1.18mm, 212μm<∅<2.36mm and ∅<2.36mm). Class M sand was replaced with 25%, 50% and 75% of coarse fractions of MSWI-BA. Mix proportions for the tests undertaken are given in the testing section.

The preparation of mixes, which involves mixing, casting and curing, was explained in Chapter 3.

6.2.3 Testing

6.2.3.1 Compressive Strength

The preparation of mortars and the determination of compressive strength were carried out in accordance with the recommendations given in BS EN 196-1 (**11**) and BS 1881 Part 116 (**12**).The compressive strength of mortars were tested using cube specimens of 50mm in size. After de-moulding specimens were cured in water tanks at 20°C until testing took place. The compressive and relative strengths were calculated as described in Chapter 3 and the average of three cubes was reported.

Compressive testing was conducted for the following series:

1. **Series 1:** *Replacing cement with fine fractions of MSWI-BA.* The purpose of this series was to identify if the fractions of MSWI-BA with grain diameters below 1.18mm, 600µm 300µm, 212µm and 150µm exhibit pozzolanic reactivity. The fly ash activity index test according to BS EN 450:1995 (**13**) was used as indicator of pozzolanic reactivity and/or other characteristics (i.e. filler effect, hydraulicity) of these fractions. The activity index is defined by the ratio of the compressive strength of mortar containing 75% of cement and 25% of replacement material (MSWI-BA) as binders, to the compressive strength of the reference mix at the same age. The lower limits of activity index for fly ash given in BS EN 450:1995 are 75% and 85% at 28 and 90 days respectively. The w/b ratio was 0.5 for all mixes. The aggregates used consisted of 100% Class M sand.

Table 6.1 shows the mix proportion details that were used to examine the activity index for the different fraction of MSWI-BA. The mix number and identification are shown in columns one and two respectively. Mix identification (ID) for 100% cement as binder is always identified as the reference, ref., whereas ID for mixes containing MSWI-BA symbolises the particle diameters of the fraction examined. Columns 3 and 4 provide the proportion of different materials in the binder.

Table 6.1. Mix proportion of mortars containing different fractions of MSWI-BA as a partial replacement of cement

Mix Number	Mix ID	Binder (% in weight)	
		Cement	MSWI-BA
1	Ref.	100	0
2	Ø<150μm	75	25
3	Ø<212μm	75	25
4	Ø<300μm	75	25
5	Ø<600m	75	25
6	Ø<1.18mm	75	25

2. **Series 2**: *Replacement of cement with fractions of MSWI-BA with Ø<212μm and Ø<300μm.* Series 2 aimed to examine the long-term strength development for mixes containing various replacements levels of cement with MSWI-BA with either Ø<212μm and Ø<300μm. Cement was replaced with increasing MSWI-BA content from 0 to 50%. The w/b ratio was 0.5 for all mixes. Aggregates included 100% of class M sand. Table 6.2 provides mix details for series 2. Mix identification (ID) shown in column 2 symbolises the particle size of the MSWI-BA fraction examined and the cement replacement level used for the mix.
3. **Series 3:** *Replacement of cement with 25% of silica sand with particle diameter below Ø<212μm.* The silica sand was used as an inert material, so the influence of MSWI-BA as pozzolanic material could be evaluated. Table 6.3 shows mix proportion for this series. The w/b ratio was 0.5 for all mixes. Aggregates included 100% of class M sand.
4. **Series 4:** *Replacing sand with coarse fractions of MSWI-BA.* This series consisted of replacing class M sand with coarse fractions of MSWI-BA with particle sizes of 212μm<Ø<2.36mm, 212μm<Ø<1.18mm and Ø<2.36mm. Class M sand was replaced with 0, 25, 50 and 75% of the coarse MSWI-BA fractions. Coarse fractions were always referred to the MSWI-BA fractions used as a partial replacement of sand throughout this experimental programme. The binder for this series consisted of 100% cement. The w/b ratio was 0.5 for all mixes. Table 6.4 provides the mix proportions for mortars containing MSWI-BA. The mix identification symbolises the particle diameters of the MSWI-BA fraction used for this mix as partial replacement of sand.

Table 6.2. Mix proportions for mortar containing MSWI-BA with Ø<212μm and Ø<300μm as partial replacement of cement

Mix Number	Mix ID	Binder (% in weight)	
		Cement	MSWI-BA
7	Ref.	100	0
8	Ø<212μm(10)	90	10
9	Ø<212μm(20)	80	20
10	Ø<212μm(30)	70	30
11	Ø<212μm(40)	60	40
12	Ø<212μm(50)	50	50
13	Ø<300μm(10)	90	10
14	Ø<300μm(20)	80	20
15	Ø<300μm(30)	70	30
16	Ø<300μm(40)	60	40
17	Ø<300μm(50)	50	50

Table 6.3. Mix proportion for mortar containing 25% silica sand with Ø<212μm as partial replacement of cement

Mix Number	Mix ID	Binder (% in weight)	
		Cement	Silica sand
18	SS Ø<212μm	75	25

5. **Series 5**: *Influence of using a w/b ratio of 0.6.* This series examined the effect of increasing w/b ratio on compressive strength for mixes containing various replacement levels of sand with MSWI-BA with 212μm<Ø<2.26mm. Binders consisted of 100% cement. The w/b ratio was 0.6 for all mixes of this series. Sand replacement levels used for this series were 0, 25, 50 and 75%. Table 6.5 show mix proportions for this series.

6. **Series 6**: *Replacing cement and class M sand with MSWI-BA.* This series examined the effect of replacing cement and sand on compressive strength. Cement was partially replaced with 0, 15 and 30% of MSWI-BA with Ø<212μm and sand was partially replaced with 0, 25 and 50 % of MSWI-BA with 212μm<Ø<2.36mm. The w/b ratio was 0.5 for this series. Table 6.6 shows the mix proportions of binder and aggregates. Mixes are identified by the percentage of

cement (C) in the binder and percentage of class M sand (S) in aggregates. For example, mix $C_{85\%}$-$S_{75\%}$ represents a mix that include the binder containing 85% of cement and 15% of MSWI-BA with Ø<212μm and the aggregates containing 75% of class M sand and 25% of MSWI-BA with 12μm<Ø<2.36mm.

Table 6.4. Mix proportion for mortar containing various fractions of MSWI-BA as replacement of sand

Mix Number	Mix ID	Aggregates (% in weight)	
		Class M Sand	Fraction of MSWI-BA
19	Ref.	100	
20	212μm<Ø<2.36mm	75	25
21	212μm<Ø<2.36mm	50	50
22	212μm<Ø<2.36mm	25	75
23	212μm<Ø<1.18mm	75	25
24	212μm<Ø<1.18mm	50	50
25	212μm<Ø<1.18mm	25	75
26	Ø<2.36mm	75	25
27	Ø<2.36mm	50	50
28	Ø<2.36mm	25	75

Table 6.5. Mix proportion of mortars containing various replacement levels of sand with MSWI-BA with 212μm<Ø<2.26mm using a w/b ratio of 0.6

Mix Number	W/B	Aggregates (% in weight)	
		Class M Sand	212μm<Ø<2.26mm
29	0.6	100	
30	0.6	75	25
31	0.6	50	50
32	0.6	25	75

Table 6.6. Mix proportions for mortar containing MSWI-BA with Ø<212μm as replacement of cement and MSWI-BA with 212μm<Ø<2.36mm as replacement of sand

Mix number	Mix ID	Binders (% in weight)		Aggregates (% in weight)	
		Cement	Ø<212μm	Class M Sand	212μm<Ø<2.36mm
33	Ref.	100	0	100	0
34	$C_{85\%}$-$S_{100\%}$	85	15	100	0
35	$C_{70\%}$-$S_{100\%}$	70	30	100	0
36	$C_{100\%}$-$S_{75\%}$	100	0	75	25
37	$C_{85\%}$-$S_{75\%}$	85	15	75	25
38	$C_{70\%}$-$S_{75\%}$	70	30	75	25
39	$C_{100\%}$-$S_{50\%}$	100	0	50	50
40	$C_{85\%}$-$S_{50\%}$	85	15	50	50
41	$C_{70\%}$-$S_{50\%}$	70	30	50	50

6.2.3.2 Saturated Density

The saturated density (ρ_s) was evaluated in accordance with BS EN 1881-114: 1983 (**14**). The saturated density is defined as the ratio of the saturated mass of the specimen to its volume (Equation 6.1). The saturated mass was measured by weighing the specimen after saturating in water. The volume was determined by the displacement of water following Equation 6.2.

$$\rho_s = \left[\frac{m_a}{V}\right] \qquad \textbf{Equation 6.1}$$

$$V = \left[\frac{m_a - m_w}{\rho_w}\right] \qquad \textbf{Equation 6.2}$$

m_a= mass of the saturated specimen in air after wiping off excess water, in kg.

V= volume of the specimen determined by the water displacement, in m^3.

ρ_s= is saturated density, in kg/m^3.

m_w= apparent mass of specimen when is fully immersed in a water tank, in kg.

ρ_w= density of water, in kg/m^3.

Saturated density was determined on 50mm*50mm*50mm in size for the mixes shown in table 6.6.

6.2.3.3 Drying Shrinkage

Drying shrinkage was performed in accordance with BS 1881-206:1986 (**15**) and measured on prisms with dimensions 75mm*75mm*300mm. Prisms were cast and cured for 24 hour as described in Chapter 3. After de-moulding, two demec studs, at a

spacing of 200mm, were attached to the four longitudinal faces of each prism. The prisms were then placed in air at 20°C ± 1°C and 65% RH for the duration of the test. The change in length between the two stubs was monitored by using a gauge. Length change was carried out on two prisms from the same batch and the average of the eight sides (four sides of each prism) was reported. The drying shrinkage is expressed in terms of micro-strains (μ_s) which were calculated as was mentioned in Chapter 3.

Length change was tested for two experimental series;

1. **Series 1**: *Replacing of cement with fractions of MSWI-BA with Ø<212μm and Ø<300μm.* This series examined the effect of replacing cement with MSWI-BA with Ø<212μm and Ø<300μm on drying shrinkage. The replacement levels ranged from 0% to 50% of MSWI-BA (see section 6.2.3.1 Table 6.2).
2. **Series 2**: *Replacing of cement with MSWI-BA with Ø<212μm and sand with MSWI-BA fraction with 212μm<Ø<2.36mm.* This series examined the effect of replacing cement and sand with MSWI-BA on drying shrinkage. Replacement levels range from 0 to 20% in binders and from 0 to 50% in aggregates.. The w/b ratio was 0.5 for all mixes. Table 6.7 provides mix proportion for mortar containing MSWI-BA as replacement of cement and sand.

Table 6.7. Mix proportion for mixes containing MSWI-BA as partial replacement of cement and sand

Mix Number	Mix ID	Binders (% in weight)		Aggregates (% in weight)	
		Cement	Ø<212μm	Class M sand	212μm<Ø<2.36mm
42	Ref.	100	0	100	0
43	$C_{90\%}$-$S_{75\%}$	90	10	75	25
44	$C_{85\%}$-$S_{75\%}$	85	15	75	25
45	$C_{80\%}$-$S_{75\%}$	80	20	75	25
46	$C_{90\%}$-$S_{50\%}$	90	10	50	50
47	$C_{85\%}$-$S_{50\%}$	85	15	50	50
48	$C_{80\%}$-$S_{50\%}$	80	20	50	50

6.2.3.4 Flexural and Equivalent Cube Strengths

The flexural strength was tested in accordance with BS EN 12390 (**16**). Flexural test was carried out on the same prisms (75mm*75mm*300mm) that were used to determine drying shrinkage. The average of two prisms was reported. Determination of flexural strength was given in Chapter 3.

The equivalent cube strength was carried on the broken portions of prisms in accordance with BS 1881. part 119.1983 (**17**). The average of four portions was taken to represent the equivalent cube strength.

Testing of flexural and equivalent cube strength was conducted at 900 days for mixes containing MSWI-BA as replacement of cement and 720 days for mixes containing MSWI-BA as replacement of cement and sand. Mix details and proportions are already provided in section 6.2.3.3 and Table 6.7.

6.2.3.5 Porosity

Total pore volume (TPV) and relative pore volume (RPV) were determined using mercury intrusion porosimetry (MIP). Details of the MIP technique, instrument and experimental parameters used have been given in Chapter 3. The mortar samples subjected to MIP testing were taken from crushed cubes that were used for the compressive strength test (see compressive strength series 6). Cement was partially replaced with the MSWI-BA fraction with Ø<212μm, whilst Class M sand was replaced with the fraction of MSWI-BA with 212μm<Ø<2.36. Mix proportions are shown in Table 6.6.

6.3 RESULTS AND DISCUSSION

6.3.1 Compressive Strength

6.3.1.1 Replacing of Cement with Fine Fractions of MSWI-BA

Figure 6.1 shows the relative strength for mortars containing fractions of MSWI-BA with particle diameters (Ø) below 1.18 mm, 600μm 300μm, 212μm and 150μm as a partial cement replacement. Relative strength is defined as the ratio of the strength of mix containing 25% of MSWI-BA as partial cement replacement to the strength of reference mix strength at the same age.

At 28 days, the relative strengths of mortars containing MSWI-BA with Ø<300μm, Ø<212μm and Ø<150μm were approximately 70%, which were closed to the minimum (75%) recommended for fly ash according to BS EN 450 (**13**). At 90 days, the relative strengths of the mixes containing MSWI-BA were significantly lower than the minimum relative strength (85%) recommended in BS EN 450. Hence, the mixes containing MSWI-BA with Ø<212μm and Ø<150μm exhibited relative strengths approximately 70% at 90 days, whereas the relative strengths of mixes containing the fractions of MSWI-BA Ø>212μm were 60% approximately. Therefore, activity index test results indicated that the fractions of MSWI-BA examined did not develop the required compressive strength for fly ash used in concrete. The lower relative strengths of

mortar containing MSWI-BA compared with EN BS 450 fly ash can be explained as a result of the coarser particle size of MSWI-BA examined and/or lack of pozzolanic reactivity. In general, the particle sizes of cement and blending materials are equal or lower than 45μm-35μm, whereas the finest particle sizes examined were below 150μm.

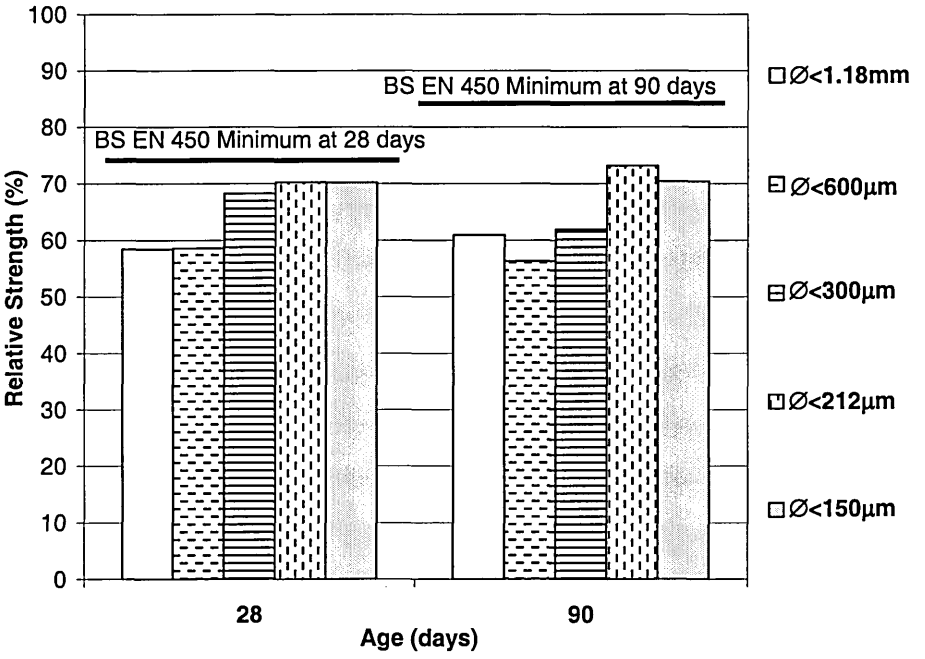


Figure 6.1. Activity index in accordance with BS EN 450 for mortar containing 25% cement replacement with MSWI-BA with various particle sizes

The results showed that as the particle size of MSWI-BA fractions was finer the contribution to strength was higher. This phenomenon, it has been widely observed for pozzolanic materials (e.g. fly ash), which has shown a significant increase in strength as fineness or surface area increases (**18**). Additionally, the increase in strength with de decrease of MSWI-BA particle diameter can be as a result of a better packing.

Since the relative strength of mortar containing MSWI-BA fractions with diameters below 212μm and 300μm were similar at 28 days but they differed at 90 days, new series (Series 2) was proposed and carried out to examine the long-term compressive strength testing for both fractions. The cement was replaced with increasing proportion of both fractions ranging from 0% to 50%.

Figure 6.2 shows the development of compressive strength of mortar containing various levels of replacement of cement with the fractions of MSWI-BA with Ø<300μm and Ø<212μm. There was a systematic decrease in strength as the replacement level of cement with MSWI-BA increases. Mortar containing MSWI-BA with particle Ø<212μm exhibited higher strength development than those containing the fraction with Ø<300μm at the same replacement level. For example, at 10% MSWI-BA content,

the fraction with Ø<212μm caused a reduction in strength of approximately 5N/mm^2 compared with the reference mix at one year, whereas the fraction with Ø<300μm caused a reduction in strength of approximately 15N/mm^2 at the same replacement level and age.

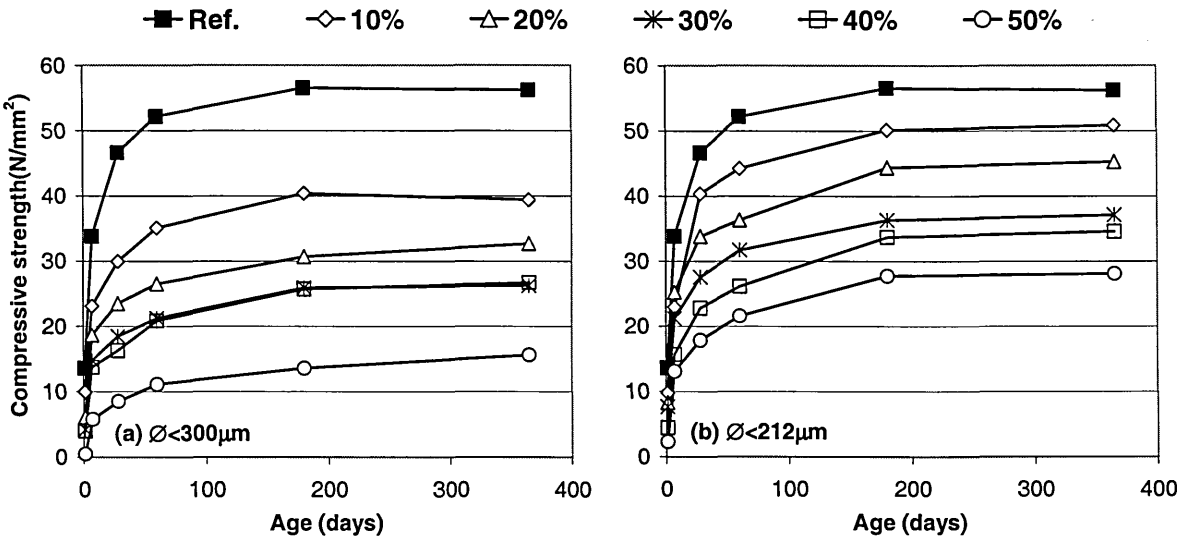


Figure 6.2. Compressive strength, N/mm^2, of mortar containing the fractions of MSWI-BA with Ø<300μm (a) and Ø<212μm (b), as partial replacement of cement

The difference in strength between mortars containing the two different fractions of MSWI-BA was associated initially with their different chemical compositions and particle size. Fraction with Ø<212μm had higher content of CaO than the fraction with Ø<300μm whereas fraction with Ø<300μm had higher content of SiO_2 (see Chapter 4 section 4.3.5). The high lime content can be associated with cementitious materials that possessed high strength development at early stage whilst high silicate content can be associated with pozzolanic materials, which can reach similar strength than cementitious materials but at long-term. However, one year mixes containing MSWI-BA with Ø<300μm did not reach the same compressive strength than mortar containing MSWI-BA with Ø<212μm. Therefore, the difference in particle size seemed to be the cause of the different strength development between both fractions.

In addition, the mortar containing 30% and 40% of MSWI-BA with Ø<300μm, showed similar compressive strength values at all ages. For MSWI-BA with Ø<212μm, the difference in strength between 30% and 40% replacement levels was also not significant.

Figure 6.3 shows compressive strength development for mortar that contained 25% cement replacement with either MSWI-BA with Ø<212μm or silica sand with Ø<212μm. It was observed that the compressive strength of mortar containing MSWI-BA was

approximately 5N/mm^2 higher than that containing silica sand (SS). Assuming that the silica sand is inert, the results indicated that MSWI-BA with∅<212μm had made a greater contribution to the strength. This can be attributed to possible pozzolanic and/or hydraulic reactivity of MSWI-BA if is assumed that both material (silica sand and MSWI-BA) had similar packing effect.

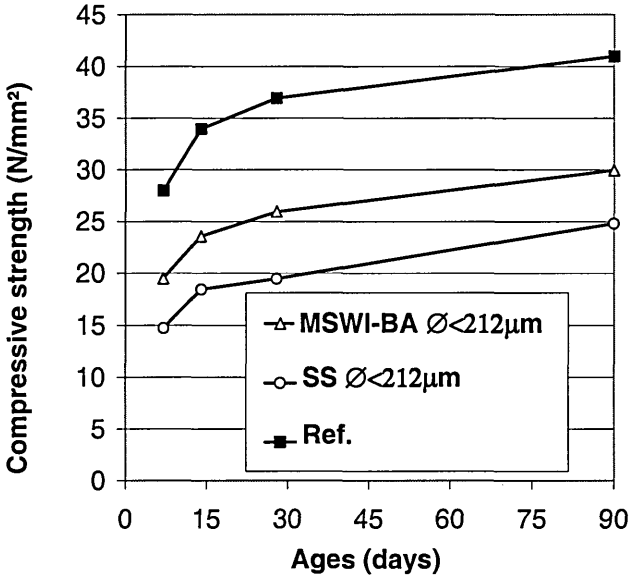


Figure 6.3. Compressive strength development of mortar containing 25% either MSWI-BA or silica sand as a partial replacement of cement

6.3.1.2 Replacing Sand with Coarse Fractions of MSWI-BA

Figure 6.4 presents the relative compressive strengths of mortar containing three fractions of MSWI-BA used as replacement of sand, at different curing times (i.e. 7, 28 and 90 days) and replacement levels (i.e. 25, 50 and 75%). The fractions of MSWI-BA examined contained particles with 212μm<∅<1.18mm, 212μm<∅<2.36mm and ∅<2.36mm.

In general, there was a decrease in strength as the replacement level of aggregates with the different fractions of MSWI-BA increases. At 25% MSWI-BA replacement level and at different curing times examined, the relative strengths of all fractions examined were nearly 100%, indicating that the strengths were similar to the reference mix. At 50% replacement level, the fraction with 212μm<∅<2.36mm still gave relative strengths nearly to 100% for the three different curing times. Thus, replacing 25% of aggregates with MSWI-BA with 212μm<∅<2.36mm did not cause a noticeable decrease in the strength development. However, there was a significant decrease in strength compared with the reference mix when 50% of class M sand was replaced with MSWI-BA with 212μm<∅<1.18mm and ∅<2.36mm. Replacing class M sand with

75% of MSWI-BA caused a significant reduction in strength for all fractions examined.

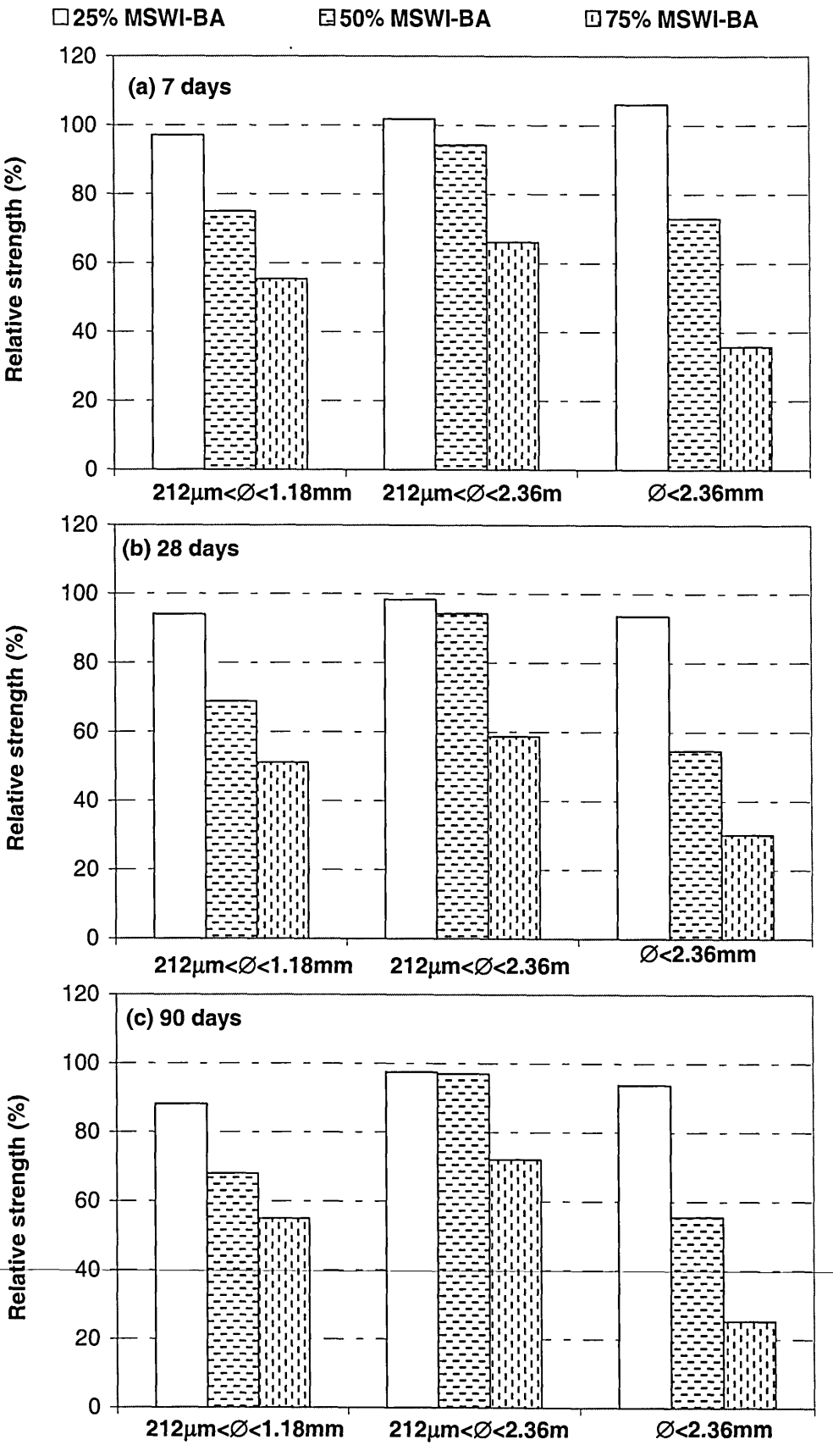


Figure 6.4. Relative compressive strength of mortar containing 25, 50 and 75% of MSWI-BA as replacement of sand at (a) 7 days, (b) 28 days and (c) 90 days

6.3.1.2.1 Effect of water to binder ratio

Figure 6.5 shows the compressive strength development of mortar containing 25, 50 and 75% of MSWI-BA as partial replacement of class M sand, at water to binder (w/b) ratios of 0.5 and 0.6. The MSWI-BA had particle with 212μm<∅<2.36mm.

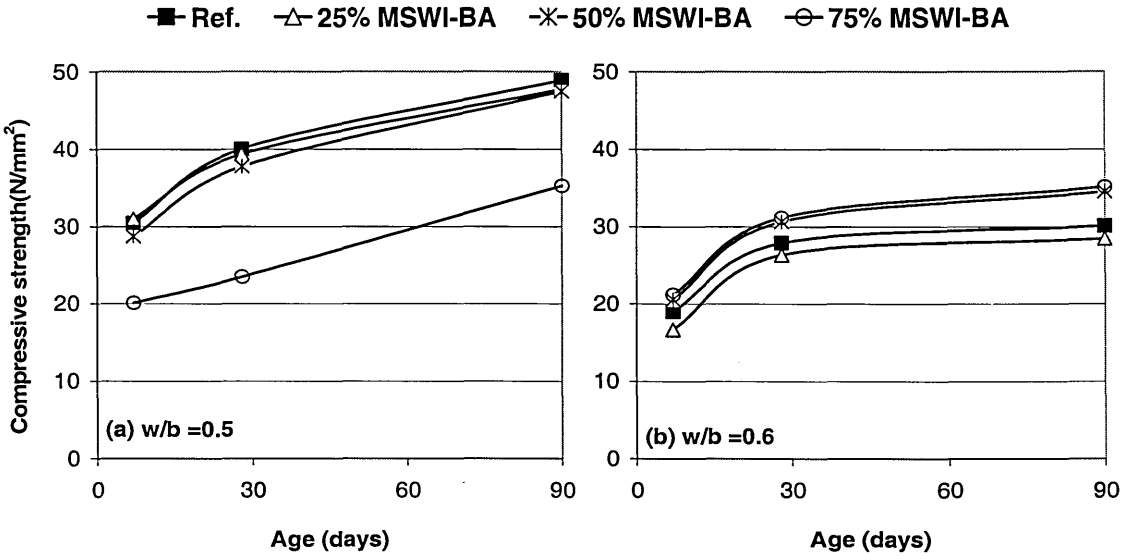


Figure 6.5. Effect of w/b ratio on mortar containing 0, 25, 50 and 75% of MSWI-BA with 212μm<∅<2.36mm as replacement of sand

As can be expected, a decrease in compressive strength was observed as w/b ratio increases from 0.5 to 0.6, at the same replacement levels. However, mixes containing 75% of MSWI-BA exhibited similar strength for both w/b ratios at 90 days.

For all replacement levels, the ratio of strength increase between 28 and 90 days was higher at w/b of 0.5 compared with that at 0.6. Using a w/b ratio of 0.6 the compressive strength of all mixes examined did not increase significantly between 28 and 90 days whereas the compressive strength of all mixes increased by approximately 10 N/mm^2 at w/b ratio of 0.5 during same curing period.

6.3.1.3 Replacing Cement and Sand with MSWI-BA

Figure 6.6 shows compressive strength of mortar containing various replacement levels of MSWI-BA used as partial replacement of cement and sand. Cement was replaced with 0, 15 and 30% of MSWI-BA with ∅<212μm. Also sand was replaced with 0, 25 and 50% of MSWI-BA with 212μm<∅<2.36mm. The nomenclature used to identify mixes in the figure represents the contents, in percentage terms, of the cement (C) and the sand (S). For example, $C_{85\%}$-$S_{50\%}$ represents a mix containing a binder with 85% cement and 15% of the fine fraction of MSWI-BA (∅<212μm) and aggregates which consisted of 50% class M sand and 50% coarse fraction of MSWI-BA

(212μm<∅<2.36mm). The reference mix always contains 100% of cement in the binder and 100% of class M sand as aggregate.

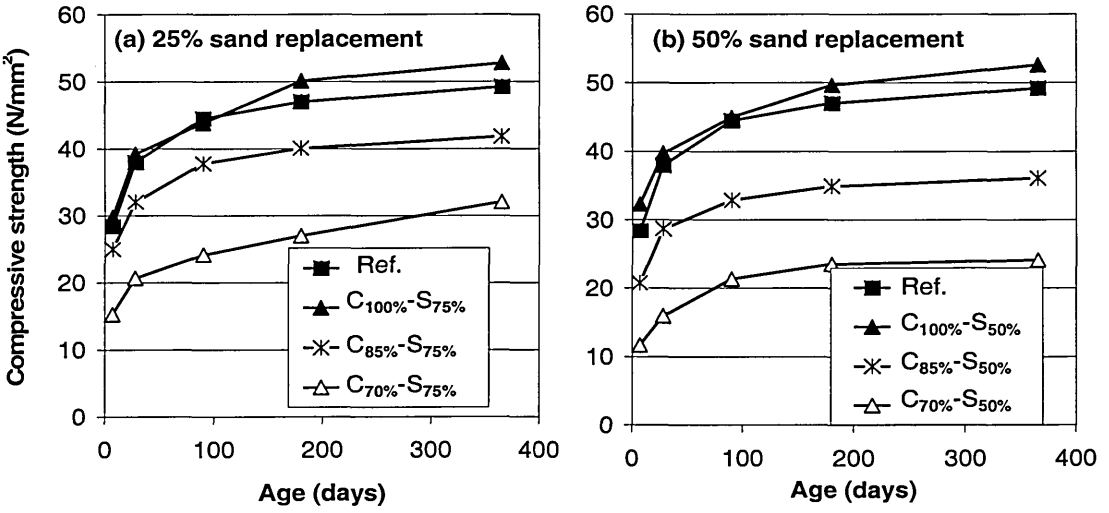


Figure 6.6. Compressive strength of mortar containing 0, 15 and 30% of MSWI-BA as replacement of cement and either (a) 25% or (b) 50% of MSWI-BA as replacement of sand

Mixes containing 25% and 50% ($C_{100\%}S_{75\%}$and $C_{100\%}S_{50\%}$) sand replacement exhibited similar compressive strength that surpassed the reference mix (ref.) at 400 days. However, as mentioned previously replacing cement with MSWI-BA caused a decrease in strength compared with the reference mix. This decrease was higher at 50% sand replacement than that at 25% for the same cement replacement level.

6.3.1.3.1 Effect of curing

The influence of curing type on compressive strength was investigated on a mix containing 15% and 50% MSWI-BA ($C_{85\%}$-$S_{50\%}$) as replacement of cement and aggregate respectively. Two curing methods were evaluated; water curing at 20°C ± 1°C and mist curing at 20°C and 95 ± 5% RH. Further details about the curing methods are explained in Chapter 3. Figure 6.7 shows strength development for the mix $C_{85\%}$-$S_{50\%}$ using water and mist curing methods.

Mix subjected to mist curing possessed slightly higher strength than this subjected to water curing. However, the difference in compressive strengths varied no more than 5N/mm^2 between both curing methods.

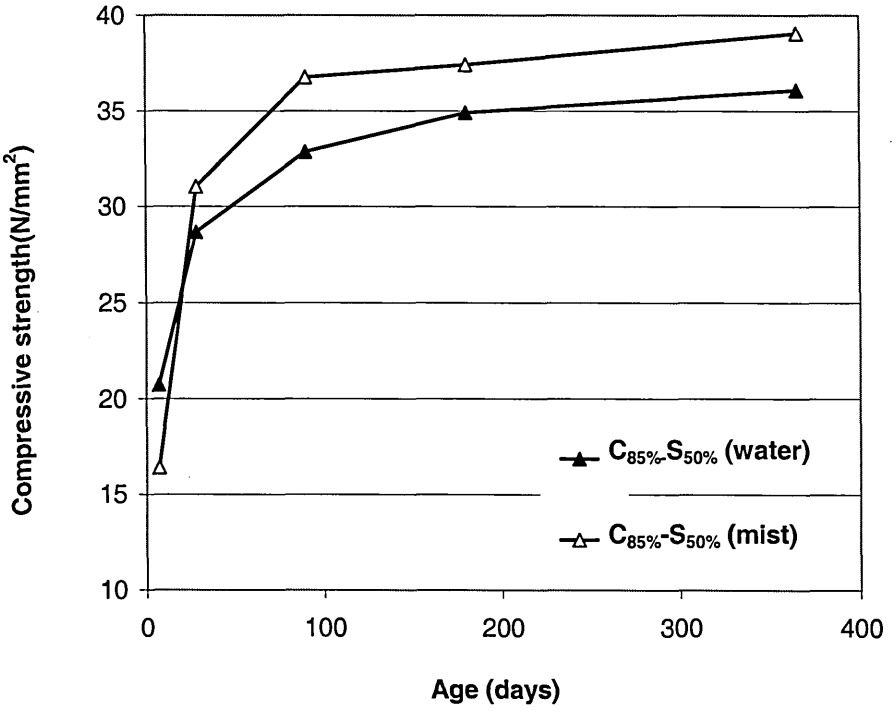


Figure 6.7. Influence of curing method on the strength of a mix containing 15% and 50% of MSWI-BA as replacement of cement and sand respectively

6.3.2 Saturated Density

Table 6.8 provides the saturated density for mortar specimens cured in water at 20°C. Saturated density was measured at 7, 28, 90, 180 and 365 days. Columns 2 and 3 provide the percentage of cement and class M sand in the binder and the aggregates respectively. Columns 4-8 report the saturated density at the different curing periods. MSW-BA with ∅<212μm was used a partial replacement of cement and MSWI-BA with 212μm<∅<2.36mm was used as a partial of sand.

Generally, the replacement of cement and/or sand with MSWI-BA caused a decrease in the saturated density compared with the reference mix. The difference in saturated density between the reference mix and the mixes containing MSWI-BA was approximately constant up to one year of curing. There was a systematic decrease in densities as the content of MSWI-BA as partial replacement of either cement or sand increased. Therefore, at 15% and 30% cement replacements, mixes containing 25% of MSWI-BA as replacement of sand exhibited were slightly higher than that for 50% sand replacement at same cement replacement levels. The decrease in density can be related to poor compaction of mortar containing MSWI-BA.

Table 6.8. Saturated density for mortar specimens containing various replacement levels of MSWI-BA as partial replacement of cement and/or sand

Mix Number	% Cement	% Class M sand	Saturated density kg/m^3				
			7	28	90	180	365
33	100	100	2218.8	2221.9	2209.6	2211.8	2211.8
34	85	100	2121.5	2125.9	2117.4	2117.5	2124.4
35	70	100	2111.4	2109.8	2115.7	2109.5	2107.1
36	100	75	2113.1	2113.6	2120.6	2118.5	2118.8
37	85	75	2085.8	2085.5	2092.1	2080.3	2100.4
38	70	75	2062.3	2069.3	2063.1	2083.2	2083.9
39	100	50	2113.5	2106.8	2102.4	2095.4	2091.5
40	85	50	2099.3	2076.5	2053.0	2050.4	2036.1
41	70	50	1966.3	1965.6	2005.4	1992.4	1957.9

6.3.3 Drying Shrinkage

6.3.3.1 Replacing Cement with Fine Fractions of MSWI-BA

Figure 6.8 shows the change in drying shrinkage with time for mortar containing MSWI-BA as partial replacement of cement. Cement was replaced with 0, 10, 20, 30, 40 and 50% by weight with MSWI-BA of Ø<300μm (Figure 6.8-(a)) and Ø<212μm (Figure 6.8-(b)).

For all mixes included the references mixes, the high rate of shrinkage occurred during the first 100 days, after this period shrinkage continued at a much lower rate. Approximately after 500 days, drying shrinkage remained constant up to at least 900 days.

Drying shrinkage increased as cement replacement level with MSWI-BA increased for both fractions of MSWI-BA used. In addition, a slightly higher drying shrinkage was observed for the fraction with Ø<212μm at 0, 10, 20 and 50% cement replacement compared with the fraction with Ø<300μm at the same cement replacement levels. However, this was associated with the higher shrinkage exhibited for the reference mix of MSWI-BA Ø<212μm series compares with the shrinkage exhibited for the reference mix of MSWI-BA with Ø<300μm. Therefore, it can be suggested that both fractions of MSWI-BA used as partial cement replacement exhibited similar drying shrinkage.

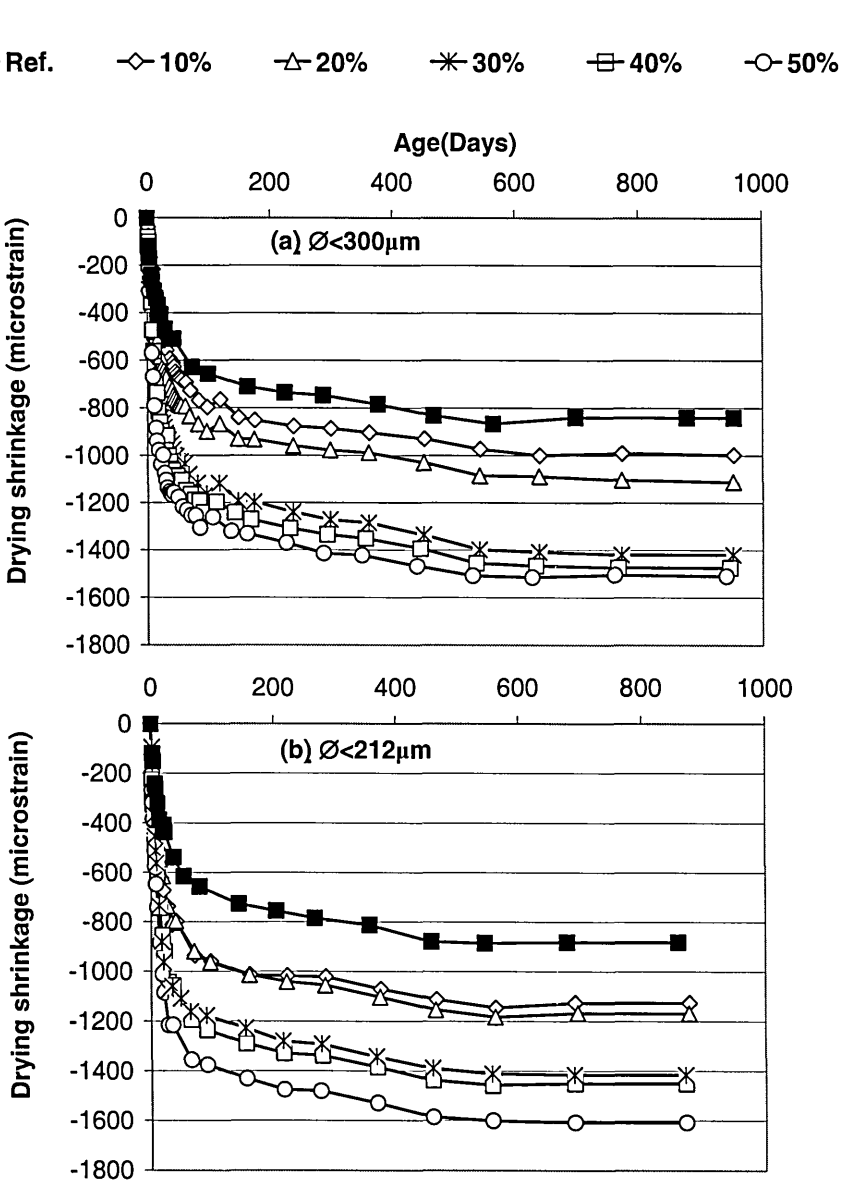


Figure 6.8. Drying shrinkage for mortar containing MSWI with (a) Ø<300μm and (b) Ø<212μm BA as a partial replacement of cement

6.3.3.2 Replacing Cement and Sand with MSWI-BA

Figure 6.9 shows the change in drying shrinkage with time for mixes containing MSWI-BA as replacement of cement and sand. Cement was replaced with 0, 10, 15 and 20% of MSWI-BA with Ø<212μm. Sand was replaced with 25% and 50% of MSWI-BA with 212μm<Ø<2.36mm.

The replacement of sand with MSWI-BA caused an increase in drying shrinkage compared with the reference mix. However, it was observed a small increase in shrinkage as MSWI-BA content in binders increased. Mixes containing 25% and 50% of MSWI-BA as sand replacement, exhibited similar drying shrinkage at the various cement replacements examined. The mixes containing 50% of MSWI-BA as sand

replacement exhibited slightly smaller drying shrinkage than the mixes containing 25% MSWI-BA at all cement replacement levels examined.

Since main factors influencing drying shrinkage (i.e. w/c ratio, cement content and chemistry, type and content of aggregates) were the same for the series containing 25% or 50% of MSWI-BA as replacement of sand, the lower shrinkage observed using 50% sand replacement may indicate that MSWI-BA could have higher restraint to the shrinkage than the class M sand (**19**). However, this did not correspond with Wainwright's (**3**) results of drying shrinkage for MSWI-BA with 600μm<∅<6mm. Wainwright reported a higher increase in drying shrinkage for mixes containing MSWI-BA compared with the reference mix

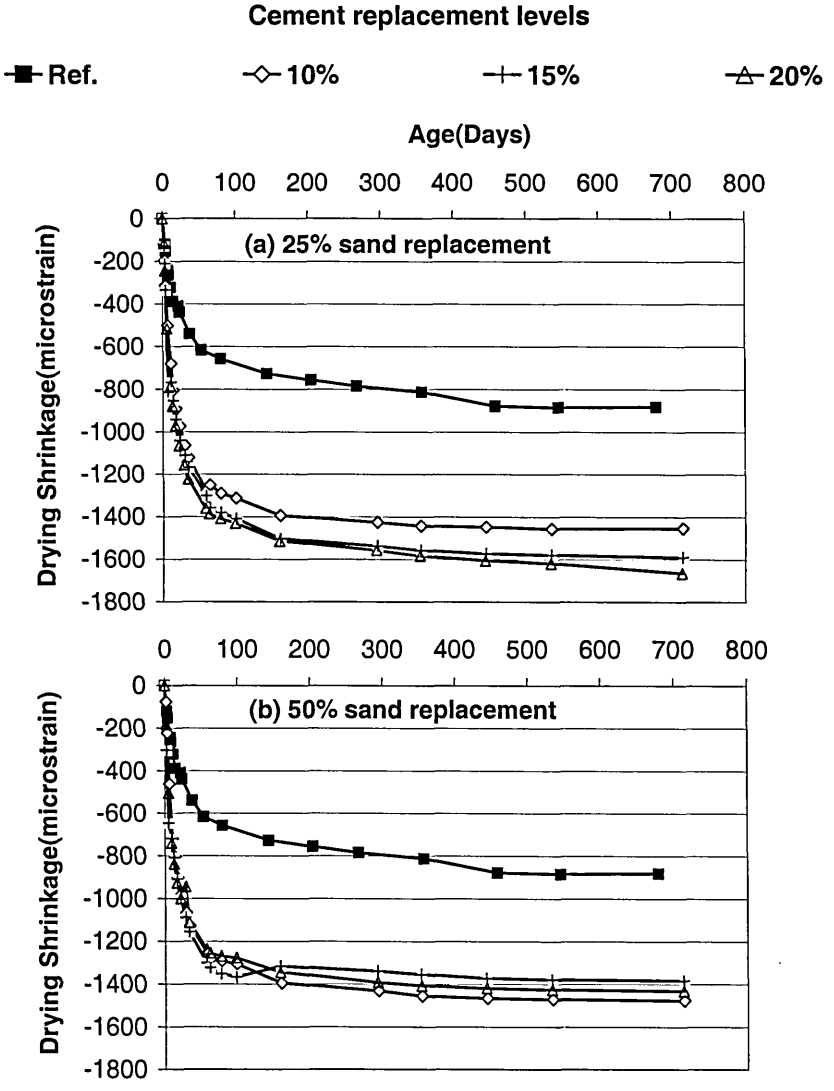


Figure 6.9. Drying shrinkage of mortar containing 0, 10, 15 and 20% of MSWI-BA with ∅<212μm as replacement of cement and (a) 25% and (b) 50% of MSWI-BA with 212μm<∅<2.36mm as replacement of sand

6.3.4 Flexural and Equivalent Cubes Strengths

6.3.4.1 Replacing Cement with the Fine fractions of MSWI-BA

Figure 6.10 shows the change in flexural (Figure 6.10-a) and equivalent cube strengths (Figure 6.10–b) at 900 days as a function of the MSWI-BA content in the binder. MSWI-BA had particles with Ø<212μm and Ø<300μm and the cement replacement levels were 0, 10, 20, 30, 40 and 50%. The figure shows that the flexural and equivalent compressive strengths for mortar containing both fractions of MSWI-BA were similar. Flexural strengths of mixes containing above 10% cement replacement were lower than for the reference mix, 0% cement replacement. The equivalent compressive strengths of mixes containing above 0% cement replacement were lower than the for the reference mix.

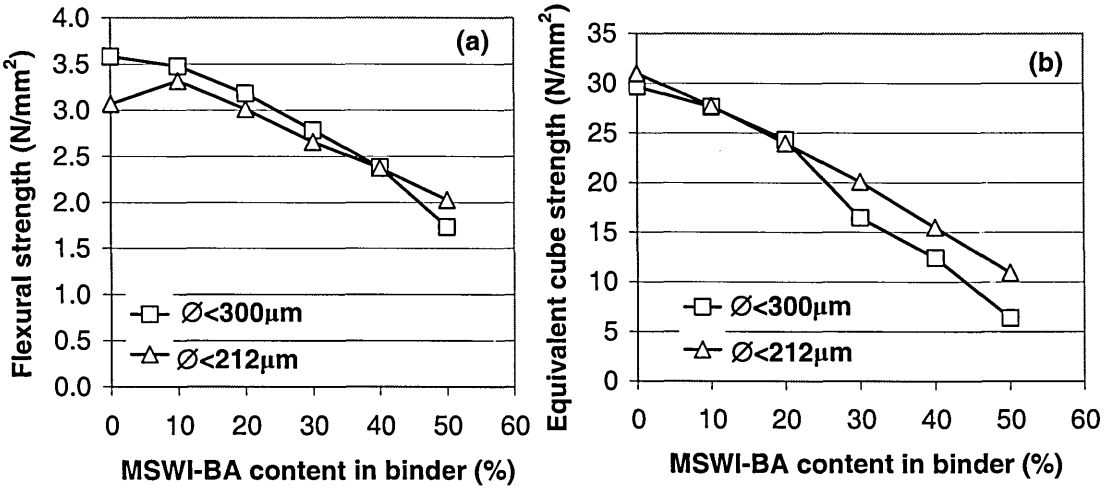


Figure 6.10. (a) Flexural and (b) equivalent cube strengths for mortar containing two fractions of MSWI-BA as replacement of cement

6.3.4.2 Replacing Cement and Sand with MSWI-BA

Figure 6.11 shows the change in flexural and equivalent cube strengths at 720 days as function of replacement level of MSWI-BA in binders. The figure compares the flexural and equivalent compressive strengths of mixes containing either 25% or 50% of MSWI-BA as replacement of sand. Both sand replacement levels exhibited similar flexural and compressive strength for the different cement replacement levels examined. Any cement replacement used decreased the flexural and equivalent cube strengths compared with the reference mix.

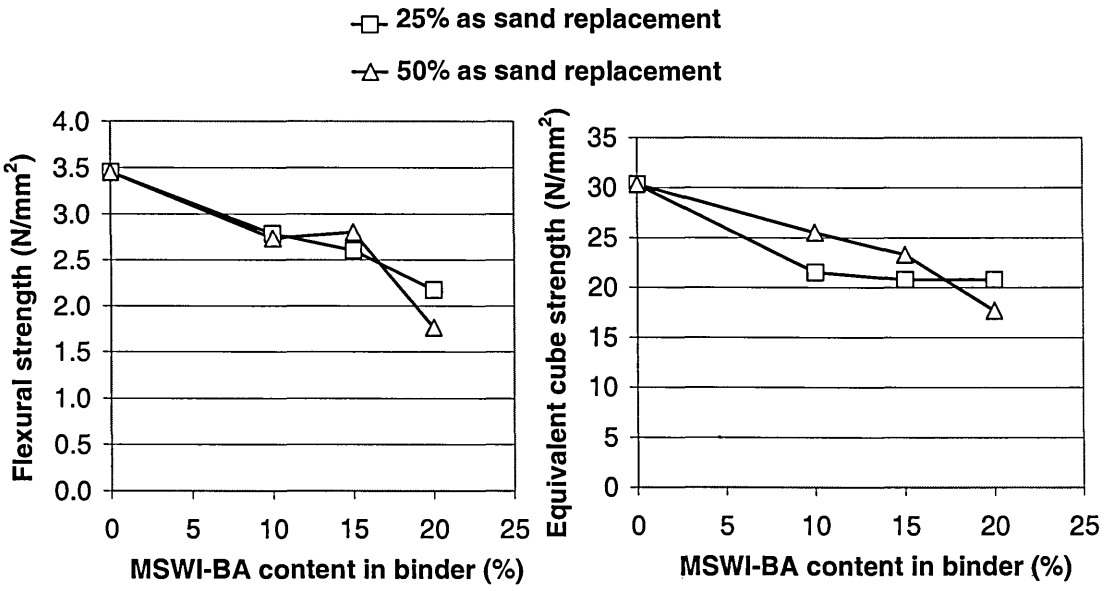


Figure 6.11. (a) Flexural and (b) equivalent cube strength for mortar containing MSWI-BA as partial replacement of cement and sand

6.3.5 Porosity and Pore Size Distribution

Porosity of and pore size distribution of mortar containing MSWI-BA was examined by using the MIP technique. Both cumulative pore volume (CPV) and relative pore volume (RPV) of mortar samples at 28 days and 180 days of curing were determined. MSWI-BA ∅<212μm and 212μm<∅<2.36mm were used as partial replacement of cement and sand respectively. The pores were split into two groups, pores with pore diameter (∅p) larger than 0.1μm (referred to as large pores) and pores with ∅p<0.1 (refereed to as small pores) (**20**).

6.3.5.1 Replacing Cement with MSWI-BA with ∅<212μm

Figure 6.12 shows the total pore volume (TPV) at 28 and 180 days of mortar containing MSWI-BA with ∅<212μm as partial replacement of cement. Cement was replaced with 0, 15 and 30% of MSWI-BA.

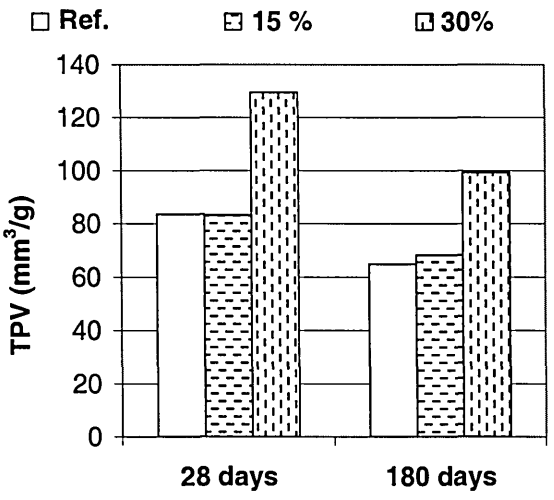


Figure 6.12. Total pore volume (TPV) of mortar containing 0, 15 and 30% of MSWI-BA with Ø<212μm as partial replacement of cement

The reference mix and the mix containing 15% MSWI-BA as replacement of cement exhibited similar TPV at 28 and 180 days. However the mix containing 30% MSWI-BA showed a substantial increase in TPV at both curing times. This increase was approximately of $40m^3/g$ at 28 days and $30m^3/g$ at 180 days of curing.

For all mixes examined in this series, it was observed that the TPV decreased approximately $20mm^3/g$ at 180 days compared with that at 28 days.

Figure 6.13 shows the percentage of (a) large pores Øp>0.1μm and (b) small pores Øp<0.1μm of mortar containing 0, 15 and 30% of MSWI-BA with Ø<212μm as replacement of cement. There was a gradual increase in percentage of large pores as MSWI-BA content in binder increased at 28 days of curing. An increase in the percentage of large pores was associated with a decrease in the percentage of small pores. At 180 days the percentages of large pores were similar at 15 and 30% cement replacement, both higher than for the reference mix. In addition, there was not a noticeable difference in either large or small pores between both curing times at 0, 15 and 30% cement replacement levels.

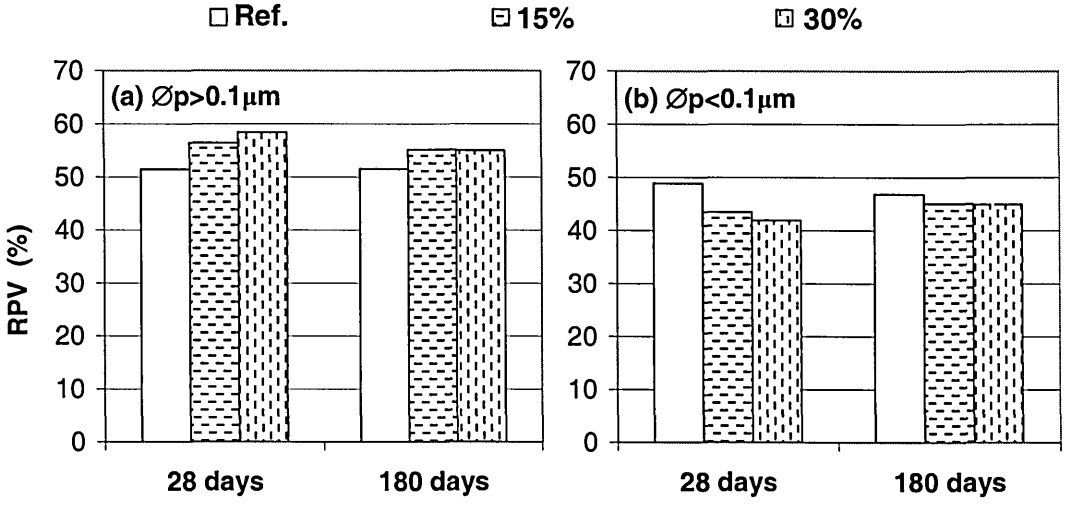


Figure 6.13. Influence of replacing 0, 15 and 30% of cement with MSWI-BA with Ø<212μm on the percentages of (a) large pores Øp>0.1μm and (b) small pores Øp<0.1μm

6.3.5.2 Replacing Sand with MSWI-BA with 212μm<∅<2.36mm

Figure 6.14 shows the total pore volume (TPV) for mortar containing partial sand replacement at 28 and 180 days of curing. Sand was replaced with 0, 25 and 50% of MSWI-BA whose grain size ranges from 212μm to 2.36mm.

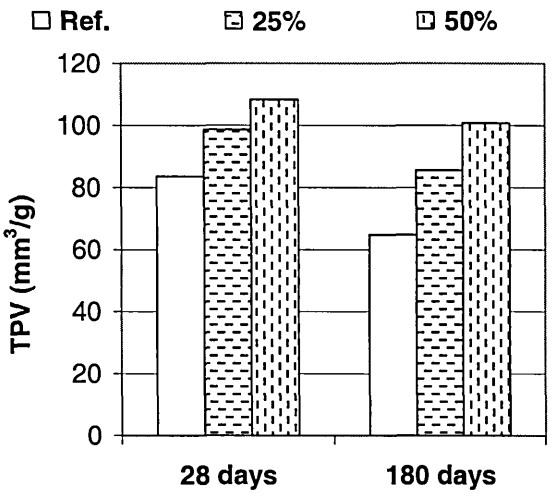


Figure 6.14. Total pore volume (TPV) of mortar containing 0, 25 and 50% of MSWI-BA with 212μm<∅<2.36mm as replacement of sand

There was a systematic increase in TPV as the MSWI-BA content increased.

For all mixes examined, it was observed that a decrease in the TPV at 180 days compared with that at 28 days. The reduction in TPV with the increase of curing time was slightly more significant for the reference mix than for the mixes containing MSWI-BA.

Figure 6.15 shows the percentage of (a) large pores ∅p>0.1μm and (b) small pores ∅p<0.1μm of mortar containing 0, 25 and 50% of MSWI-BA with 212μm<∅<2.36mm as replacement of sand.

The mixes containing 25 and 50% of MSWI-BA exhibited similar proportion of large and small pores regardless of the curing times. In addition, the mixes containing MSWI-BA as replacement of sand possessed higher proportion of large pores at 28 and 180 days of curing than the reference mix. Again, an increase in the proportion of large pores was associated with a decrease in small pores.

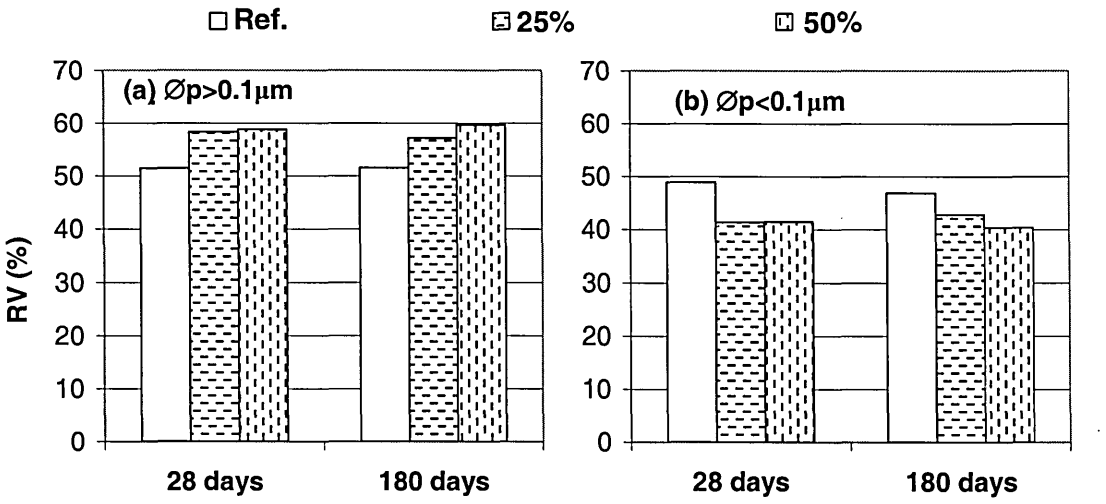


Figure 6.15. Influence of replacing 0, 25 and 50% of sand with MSWI-BA on the percentages of (a) large pores Øp>0.1μm and (b) small pores Øp<0.1μm

6.3.5.3 Replacing Cement and Sand with MSWI-BA

Figure 6.16 shows the total pore volume (TPV) at 28 and 180 days for mortar containing 0, 15 and 30% of MSWI-BA with Ø<212μm as partial cement replacement and 0, 25 and 50% of MSWI-BA with 212μm<Ø<2.36mm as sand replacement.

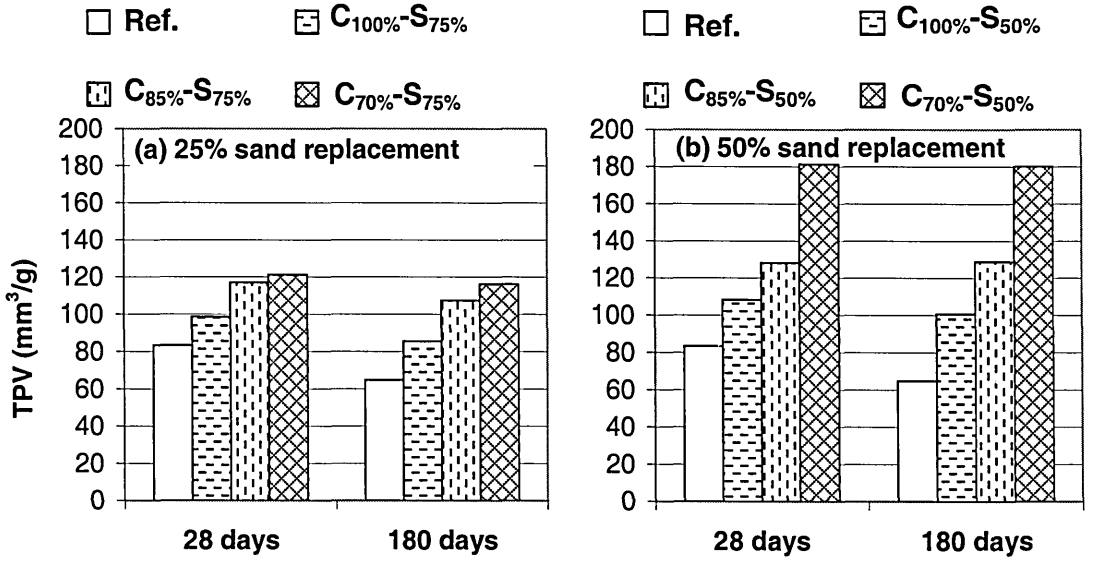


Figure 6.16. Total pore volume (TPV) of mortar containing 0, 15, 30% of MSWI-BA (Ø<212μm) as cement and (a) 25% and (b) 50% of MSWI (212μm<Ø<2.36mm) as sand

There was a gradual increase in TPV as the levels of MSWI-BA in binder and in aggregates increased. Hence, the mix containing 30% and 50% ($C_{70\%}S_{50\%}$) as cement and sand replacements respectively exhibited the highest TPV of the whole.

In addition, the reference mix and most of mixes containing 25% and 50% sand replacement and various cement replacement levels showed a small decrease in TVP at 180 days compared with 28 days of curing. This decrease in TPV with curing time was less significant as cement replacement levels increased.

Figure 6.17 shows the percentage of (a) large pores Øp>0.1μm and (b) small pores Øp<0.1μm of mortar containing 0, 15 and 30 of MSWI-BA with Ø<212μm as replacement of cement and either 25% or 50% of MSWI-BA with 212μm<Ø<2.36mm as replacement of sand.

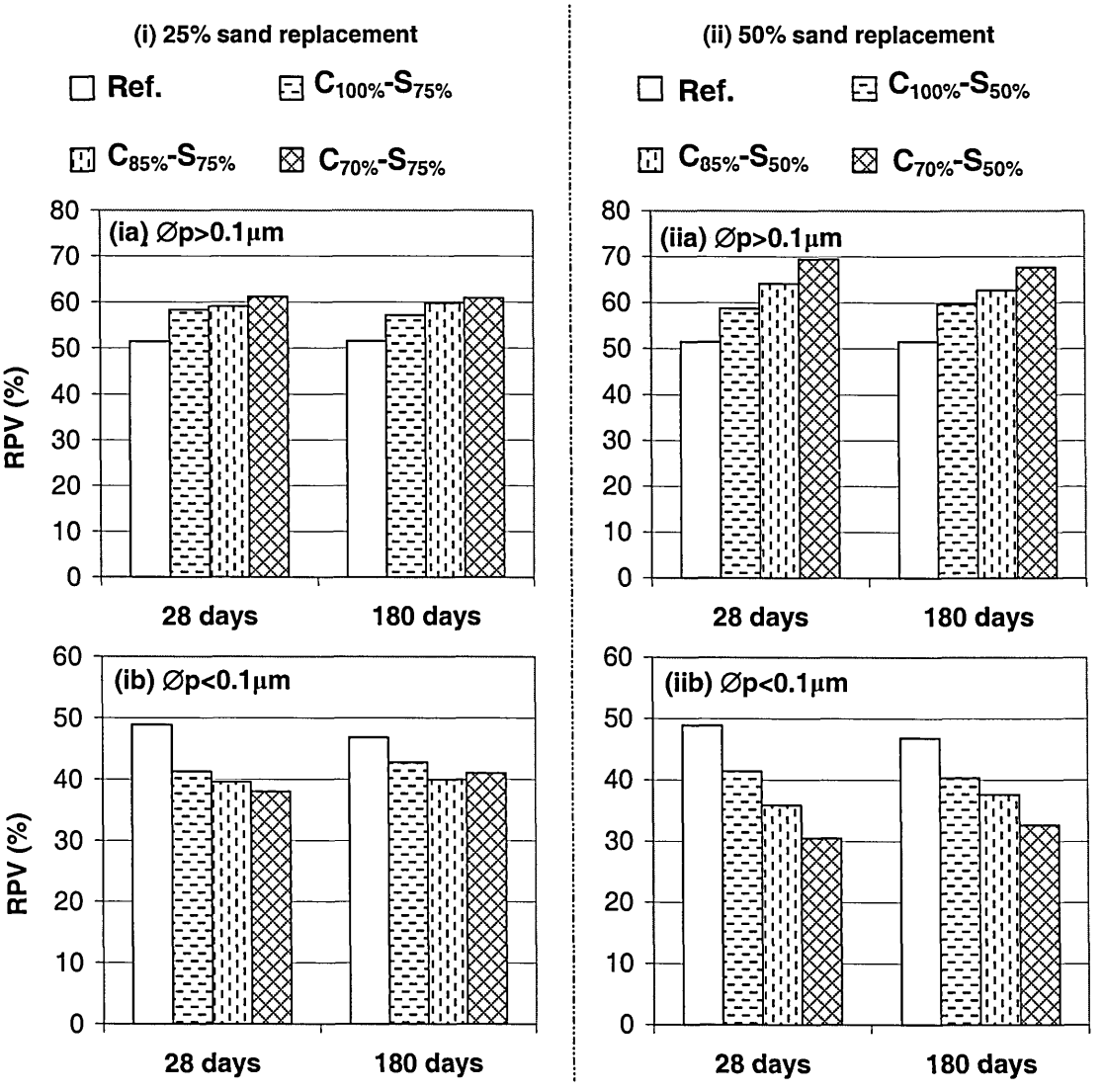


Figure 6.17. Influence of partial replacement cement with 0, 15 and 30% of MSWI-BA (Ø<212μm) and partial replacement of sand with (i) 25 and (ii) 50% of MSWI-BA (212μm<Ø<2.36mm) on percentages of (a) large pores (Øp>0.1μm) and (b) small pores (Øp<0.1μm)

In general, an increase in MSWI-BA content caused an increase in the volume of large pores and consequently a decrease in pore with ∅p<0.1μm compared with reference mix at 28 and 180 days of curing. This effect was the same than those observed when MSWI-BA was used as either replacement of cement or sand.

At 25% as sand replacement there was not significant difference in volume of large and small pores between the different cement replacement levels examined. However, at 50% as sand replacement, a gradual difference in volume of large and small pores was observed as function of cement replacement content.

In addition, it was observed that the mixes containing 15% and 30% of cement replacements and 25% sand replacement (mixes $C_{85\%}$-$S_{75\%}$ and $C_{70\%}$-$S_{75\%}$) exhibited smaller percentage of large pores than mixes containing 50% sand replacement at same cement replacement contents.

6.3.6 Strength and Porosity Relationship

Figure 6.18 shows the relationship between compressive strength and total pore volume for mixes containing MSWI-BA as a partial replacement of cement and/or sand. Mixes examined contained cement replacement levels of 0%, 15% and 30% and sand replacement levels of 0%, 25% and 50%.

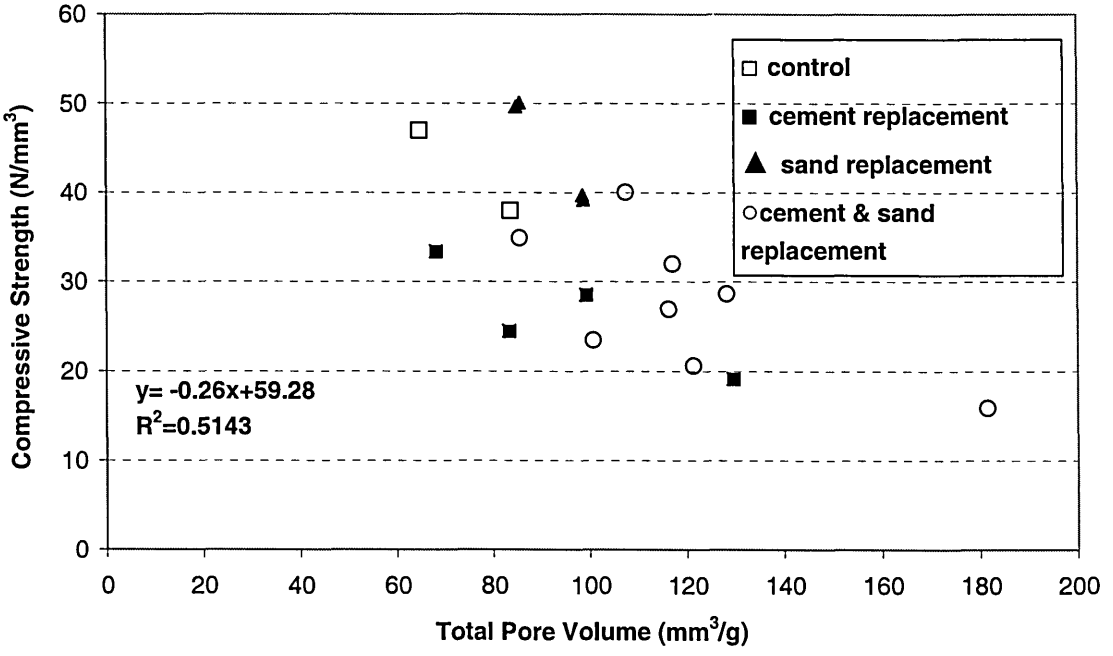


Figure 6.18. Relationship between compressive strength total pore volume

The relationship between strength and total pore volume was best expressed by a linear equation as proposed by Hasselmann (**21**). The correlation coefficient of the data set was very low. This can be attributed to the use of MSWI-BA as partial replacement of cement or sand or both. However, the well known decrease in strength as a

consequence of increasing total pore volume was observed for the different mixes examined.

6.4 CONCLUSIONS

This chapter has evaluated the influence of replacing cement and/or sand with MSWI-BA. This included the determinations of compressive strength, saturated density, drying shrinkage, flexural strength and porosity for mortars containing MSWI-BA with different particles sizes and at various cement or sand replacement levels.

The evaluation of the compressive strength development of mortars containing MSWI-BA as a partial replacement of cement or sand has been used as a key parameter to select the particle sizes of MSWI-BA that were subjected to further tests in this chapter (i.e. drying shrinkage, porosity) and in following chapters (i.e. sulfate resistance and leaching).

Results of relative strengths for mortars containing 25% of MWI-BA with particle diameters (∅) below 1.18mm, 600μm, 300μm, 212μm and 150μm as a partial replacement of cement, were all lower than the minimum required for fly ash in accordance to BS EN 450 (75% and 85% at 28 and 90 days respectively). The lower relative strengths of mixes containing of MSWI-BA were attributed to the coarser particle sizes of MSWI-BA examined compared with BS EN 450 fly ash. However, it was also found that the relative strengths of the mix containing MSWI-BA with ∅<212μm was one of the highest ones compared with other mixes containing coarser or finer particle diameters of MSWI-BA.

The compressive strength development of mortars containing 10, 20, 30 40 and 50% of MSWI-BA with either ∅<300μm or ∅<212μm as a partial replacement cement were significantly higher for mixes containing MSWI-BA with ∅<212μm than for mixes made with MSWI-BA with ∅<300μm, at all cement replacement levels. This was also attributed to the difference in particle sizes.

Moreover, comparison of compressive strengths between mixes containing either MSWI-BA with ∅<212μm or inert silica sand with the same particle size indicated a slightly higher strength development for the mix containing MSWI-BA. This suggested possible pozzolanic activity of MSWI-BA with ∅<212μm.

The examination of compressive strengths for mixes containing 25, 50 and 75% MSWI-BA with 212μm<∅<1.18mm, 212μm<∅<2.36mm and ∅<2.36mm as a partial replacement of sand showed that the mixes containing MSWI-BA with 212μm<∅<2.36mm exhibited higher strength than the other MSWI-BA examined at all replacement levels. In addition, the compressive strength of mixes containing 25% or

50% of MSWI-BA with 212μm<∅<2.36mm as a partial replacement of sand were similar and exceeded the reference mix strength. Therefore, MSWI-BA with 212μm<∅<2.36mm and either 25% and 50% sand replacement levels were selected for further testing.

The influence of replacing cement and sand with MSWI-BA with ∅<212μm and 212μm<∅<2.36mm respectively on the other properties examined in this chapter is summarised as follows:

1. Decrease in compressive strength. The decrease in compressive strength was higher for mixes containing 50% of sand replacement compared with those containing 25% sand replacement at the same cement replacement levels.
2. Decrease in saturated density as cement and sand replacement levels increased.
3. Increase in drying shrinkage as cement replacement levels increased. However, the increase in sand replacement level from 25% to 50% appeared to have less influence than the increase in cement replacement. Hence, mixes containing 25% of MSWI-BA as a partial replacement of sand exhibited higher drying shrinkage than those containing 50% as a partial replacement of sand at the same cement replacement. This was not expected due to the high absorption affinity of MSWI-BA reported in the literature review.
4. In addition, the drying shrinkages for mixes containing MSWI-BA with either ∅<300μm or ∅<212μm as cement replacement were similar, and increased as the cement replacement level increased.
5. Flexural and equivalent cube strengths decreased as the content of MSWI-BA in the binders increased. However, there was a small difference in flexural and equivalent cubes strengths as a result of using either 25% or 50% sand replacement level.
6. The replacement of cement with either MSWI-BA with ∅<300μm or ∅<212μm had small influence on flexural and equivalent cubes strengths, which increased significantly as cement replacement levels increased.
7. Total pore volume (TPV) increased as cement and sand replacement levels increased. The increase in TPV was significantly high for the mix containing 30% of MSWI-BA as a partial replacement of cement, whereas the TPV of the mix containing 15% of MSWI-BA was similar to the reference mix. The replacement of sand caused a gradual increase in TPV. Hence, mix containing 30% and 50% of MSWI-BA as partial replacement of cement and sand had the highest TPV. The TPV of all mixes examined was lower at 180 days of curing than at 90 days as

expected. The reduction of TPV with curing time was similar for all mixes including the reference mix.

8. The percentage of large pores (∅p>0.1μm) was higher for mixes containing MSWI-BA as partial replacement of cement and/or sand compared with that for the reference mix at 28 days and 180 days of curing. This suggested that there was not a refinement of the small pore as results of later formation of calcium silicate hydrates. The later calcium silicate hydrates are formed as consequence of possible pozzolanic reaction. This phenomenon has been observed on numerous occasions for binders containing fly ash and slag. was observed

6.5 REFERENCE

1 Pfrang-Stotz G. and Reichelt J. "Municipal Solid Waste Incinerator Bottom Ash: Characteristics and the Use in Road Construction". Proceedings of International Symposium "Use of Incinerator Ash". Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

2 York D.M. "MSWI Plants: Sustainable Quarries". Proceedings of International Symposium Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer and Kevin A Paine. 2000

3 Wainwright P.J., J.R. Barton and Cresswell D.J.F. "The Long-Term Performance of Untreated Bottom Ash, and the Production and Use of a Lightweight Synthetic Aggregate from the Bottom Ash Fine Fraction." Proceedings of International Symposium: Use of Incinerator ash. Edited by Ravindra K. Dhir, Tom D. Dyer ans Kevin A Paine. 2000

4 Paine K.A., Dhir R. K. and Doran V.P.A. "Unprocessed and Processed Incinerator Ash as a Cement Bound Material."Proceedings of International Symposium: Use of Incinerator Ash. Edited by Ravindra K. Dhir, Tom D. Dyer ans Kevin A Paine. 2000

5 Glasser F.P. "Properties of Cement Waste Composites". Waste Management Vol. 16, Nos, 1-3 pp. 159-168. 1996

6 Glasser F. P. "Fundamental Aspects of Cement Solidification and Stabilisation". Journal of Hazardous Materials 52 pp 151-170. 1997

7 Hill, A. R, Damson, A.R. and Muddy, M. "Utilisation of aggregates in road construction and bulk fill". Resources, Conservation Dan Recycling 32 pp305-320. 2001.

8 Neville. A. M. "Properties of Concrete". Chapter 6: Strength of Concrete. Ed. Longman Group Limited, fourth and Final Edition. 1995

9 BS 12. 1996: Specification for Portland cement

10 BS 882:1992. Specifications for Aggregates from Natural Sources for Concrete

11 BS EN 196-1:1995. Methods for testing cement. Part 1. Determination of Strength.

12 BS 1881-Part 116. 1983. Testing Concrete; Part 116; Methods for determination of compressive strength of concrete cubes.

13 BS EN 450:1995. Fly ash for concrete. Definitions, requirement and quality control.

14 BS 1881-Part 114. 1983. Testing Concrete; Part 114; Methods for determination of density of hardened concrete.

15 BS 1881. 1986: Testing concrete. Part 206: Recommendation for determination of strain in concrete.

16 BS EN 12390:2000. Testing of hardened concrete. Part 5; Flexural strength of test specimens.

17 BS 1881. 1983: Testing concrete. Part 119: Methods for determination of compressive strength using portions of beams broken in flexure.

18 Baoju L., Youjun W., Shiqiong Z. and Quanlian Y. "Influence of Ultra-Fine Fly Ash Composite on the Fluidity and Compressive Strength of Concrete". Cement and Concrete Research, Vol 30, pp 1489-1493. 2000

19 Neville. A. M. "Properties of Concrete". Chapter 9: Elasticity, Shrinkage and Creep. Ed. Longman Group Limited, fourth and Final Edition. 1995

20 Mehata P. K and Manmohan D. "Pore size distribution and permeability of hardened Cement Pastes". Proceedings of the 7th International congress of Chemistry of Cement, Vol 3 pp1-5. 1980

21 Hasselman D.P.H. "Relation between Effect of Porosity on Strength and on Young's Modulus of Elasticity on Polycrystalalline Materials". Journal of the American Ceramic Sociaty, Vol 46, pp 564-566. 1963

CHAPTER 7: SULFATE RESISTANCE OF MORTAR CONTAINING MSWI-BA

7.1 INTRODUCTION

Resistance of concrete or mortar to external sulfate attacks is an important durability parameter (**1**). Sulfate attack of concrete is a well-known phenomenon (**2**). Nevertheless, the complex nature of the attack has led to the formulation of numerous theories regarding its mechanism, some of which are conflicting (**3**).

Sulfate attack generally occurs when sulfate ions react with the hydration products, mainly calcium aluminate hydrate (C-A-H), Porlandite (CH) and calcium silicate hydrated (C-S-H). Ettringite ($3CaOAl_2O_33CaSO_432H_2O$) and gypsum ($CaSO_4$. $2H_2O$) are the primary products of the chemical reaction between a sulfate solution and cement hydration products. This fact has been recognised for a long time, although controversy exists in identifying the significance of each of these products in the ultimate deterioration of concrete (**1**). In addition, the formation of thaumasite can also occur under specific sulfate attack conditions. Chapter 2 includes a literature review on the formation of ettringite, gypsum and thaumasite, and the influence of physical and chemical parameters of concrete subjected to sulfate attack.

The benefits of using fly ash, other pozzolanic materials or slag as a partial replacement of cement to improve the sulfate resistance of concrete are well documented. The chemical composition of pozzolans is one of the key factors to evaluate their efficiency in retarding or mitigating the sulfate attack on concrete. For example, high CaO fly ashes exhibit a poor sulfate resistance whereas low CaO fly ashes (CaO less than 15%) can improve sulfate resistance (**4**,**5**). Moreover, combinations of Portland cement with slag can provide good sulfate resistance in most sulfate solutions, provided that the alumina level in the slag is less than 14%. Alternatively if the alumina content in the slag exceeds 14%, the C_3A content of the cement should not exceed 10% (**6**). The type of aluminate compound present in the cementitious systems prior to sulfate exposure is also important. Thus, the presence of ettringite as a primary aluminate compound rather than other aluminate phases (e.g. monosulfates and C-A-H) can improve the sulfate resistance (**4**). This has been attributed to the fact that initial formation of ettringite while the system is still in the plastic stage does not cause a disruption of the structure. However, latter ettringite formation causes detrimental expansion of concrete structure when the system has already reached hardened stage. Therefore, additional amount of SO_3 in the cement-based systems can facilitate the formation of ettringite during the plastic stage thereby improving the sulfate resistance of the system.

This chapter examines the sulfate resistance of mortar specimens containing various replacement levels of MSW-BA as a partial replacement of cement and/or sand exposed to Na_2SO_4 solution. In addition, the influences of the type of sulfate solution used (e.g. Na_2SO_4 or $MgSO_4$), the C_3A content in the cement used, and the duration of initial curing on the sulfate resistance have been evaluated for mixes containing 15% and 50% of MSWI-BA as a partial replacement of cement and sand respectively.

7.2 EXPERIMENTATION

7.2.1 Materials

Two types of cements were used; a standard 42.5 Ordinary Portland Cement, identified as C-1 with a C_3A content of 7.1%, and a cement with C_3A content of 11.2%, identified as C-2. Both cements conformed to BS12: 1996 (**7**). C-1 was used in almost all mixes, whereas C-2 was used only in one mix. MSWI-BA with particle diameter below 212μm (∅<212μm) was used as a partial cement replacement.

The fine aggregates used were class M sand in accordance with BS 882:1992 (**8**) and MSWI-BA with particle diameters ranging from 212μm to 2.36mm (212μm<∅<2.36mm)

The chemical and physical properties of materials used throughout this chapter are given in Chapters 3 & 4.

7.2.2 Mix Proportion

Sulfate resistance tests were carried out on mortars. The proportion of binder to fine aggregate ratio was 1:3. The water/binder was kept constant at 0.50. Cement was partially replaced with 0%, 15%, 20%, 30% and 50% of MSWI-BA with ∅<212μm. Class M sand was partially replaced with 0%, 25% and 50% of MSWI-BA with 212μm<∅<2.36mm. Details of all mixes are given in Table 7.1. Mix ID represents the percentage of cement and class M sand in the binders and fine aggregates respectively. For example, mix $C_{85\%}$-$S_{75\%}$ represent a mix containing 85% of cement and 15% of MSWI with ∅<212μm as binder and 75% of class M sand and 25% of MSWI-BA with 212μm<∅<2.36mm as fine aggregate. Reference mix, Ref. contains 100% of cement and class M sand as binders and aggregates respectively.

7.2.3 Mix Preparation

Mixing and casting of the mortar specimens were carried out as described in Chapter 3. Prisms of dimensions 40 x 40 x 160mm and cubes of 50mm in size were cast. After casting, prisms and cubes were placed in a mist curing room at 20±1°C and 95±5% RH for 24 hours. After this 24 hours at 20±1°C and 95±5% RH, all specimens were de-

moulded and wrapped in plastic bags for either 1, 27 or 89 days until immersing in the sulfate solutions.

Table 7.1. Mixes proportions used in sulfate resistance tests

Mix Number	Mix ID	Cement Type	Binders (% in weight)		Aggregates (% in weight)	
			Cement	Ø<212μm	Class M Sand	212μm<Ø<2.36mm
1	Ref.	C-1	100	0	100	0
2	$C_{85\%}$-$S_{100\%}$	C-1	85	15	100	0
3	$C_{70\%}$-$S_{100\%}$	C-1	70	30	100	0
4	$C_{50\%}$-$S_{100\%}$	C-1	50	50	100	0
5	$C_{100\%}$-$S_{75\%}$	C-1	100	0	75	25
6	$C_{85\%}$-$S_{75\%}$	C-1	85	15	75	25
7	$C_{80\%}$-$S_{75\%}$	C-1	80	20	75	25
8	$C_{70\%}$-$S_{75\%}$	C-1	70	30	75	25
9	$C_{100\%}$-$S_{50\%}$	C-1	100	0	50	50
10	$C_{85\%}$-$S_{50\%}$	C-1	85	15	50	50
11	$C_{85\%}$-$S_{50\%}$	C-2	85	15	50	50
12	$C_{80\%}$-$S_{50\%}$	C-1	80	20	50	50
13	$C_{70\%}$-$S_{50\%}$	C-1	70	30	50	50

7.2.4 Testing

After initial curing (e.g. 2, 28 or 90 days) at 20±1°C and 95±5% RH, prisms and cubes were immersed in either 5% (by weight) Na_2SO_4 or $MgSO_4$ solution for approximately 600 days. The sulfate solutions were renewed approximately every 30 days. The sulfate attack was evaluated by measuring changes in weight, length and compressive strength as well as visual observations. Prisms were used to monitor the change in length and weight whereas the cubes were to monitor the change in strength.

The reported changes in length, weight and compressive strength were calculated by averaging the changes observed in three replicated mortar specimens. More information regarding the length, weight and compressive strength tests is Chapter 3 "Materials, Techniques and Test Methods".

The visual deteriorations were evaluated using a numerical scale ranging from 0 to 6 (9). **Number 0** indicated no attack; **number 1** indicated a very slight attack; **number 2** indicated a slight attack; **number 3** indicated moderate attack; **number 4** indicated severe attack; **number 5** indicated partial disintegration and **number 6** indicated total disintegration.

Sulfate attack testing investigated the influence of the following factors:

a) **Series 1:** *Partial cement replacement.* Mortar contained 0%, 15%, 20%, 30% and 50% of MSWI-BA (∅<212μm) as a replacement of cement. Specimens were initially cured for 28 days before the exposure to Na_2SO_4 solution for approximately 600 days. This series includes mixes 1, 2, 3 and 4 (Table 7.1).

b) **Series 2.** *Partial sand replacement.* Mortar contained 0%, 25% and 50% of MSWI-BA (212μm<∅<2.36mm) as a replacement of sand. Specimens were initially cured for 28 days before the exposure to Na_2SO_4 solution for approximately 600 days. This series includes 1, 5 and 9 (Table 7.1).

c) **Series 3.** *Partial cement and sand replacements.* Mortar contained MSWI-BA as a partial replacement of cement and sand. Cement was partially replaced with 15%, 20%, 30% of MSWI-BA (∅<212μm) and sand was partially replaced with 25% and 50% of MSWI-BA (212μm<∅<2.36mm). Specimens were initially cured for 28 days before the exposure to Na_2SO_4 solution for approximately 600 days. Mixes 1 to 10 and mixes 12 and 13 in Table 7.1 are included in this series.

d) **Series 4.** *Duration of the initial curing before immersion.* Mix 10 (Table 7.1) containing 15% and 50% of MSWI-BA as a partial replacement of cement and sand respectively ($C_{85\%}$-$S_{50\%}$,) was cured initially for 2, 28 and 90 days before immersing in Na_2SO_4 and $MgSO_4$ solutions for approximately 600 days.

e) **Series 5.** *Content of C_3A in the Cement used.* Mortar containing 15% and 50% of MSWI-BA as a partial replacement of cement and sand respectively, were prepared using two types of cement; Portland cement (C-1) and a cement with high C_3A content (C-2). These mixes, $C_{85\%}S_{50\%}$ (mix10) and $C_{85\%}$-$S_{50\%}$ (mix 11), see Table 7.1, were immersed in Na_2SO_4 and $MgSO_4$ solutions after 28 days of initial curing for approximately 600 days.

7.3 RESULTS AND DISCUSSION

7.3.1 Replacing Cement with MSWI-BA

Figure 7.1 shows the length change of mortar specimens containing 0%, 15%, 30% and 50% MSWI-BA (∅< 212μm) as a partial replacement of cement immersed in Na_2SO_4 after initial curing of 28 days. It was observed that the change in length was dependent on the amount of MSWI-BA. The change in length for reference mix and the mix made with 15% replacement (Mix 1 and Mix 2) did not exceed 0.20% during the 600 days of immersion. In addition, the change in length was slight lower for Mix 2 (15% cement replacement) compared to Mix 1 after 250 days of immersion. The lower change in length of Mix 2 may suggest a possible improvement in sulfate resistance as a consequence of replacing cement with 15% of MSWI-BA (∅< 212μm). Mixes containing 30% and 50% of cement replacement (Mix 3 and Mix 4) exhibited significant increases in length change. Mix 3 and Mix 4 exhibited change in lengths above 0.2% after approximately 300 and 75 days of immersion respectively. Mix 4 totally disintegrated during the first 100 days.

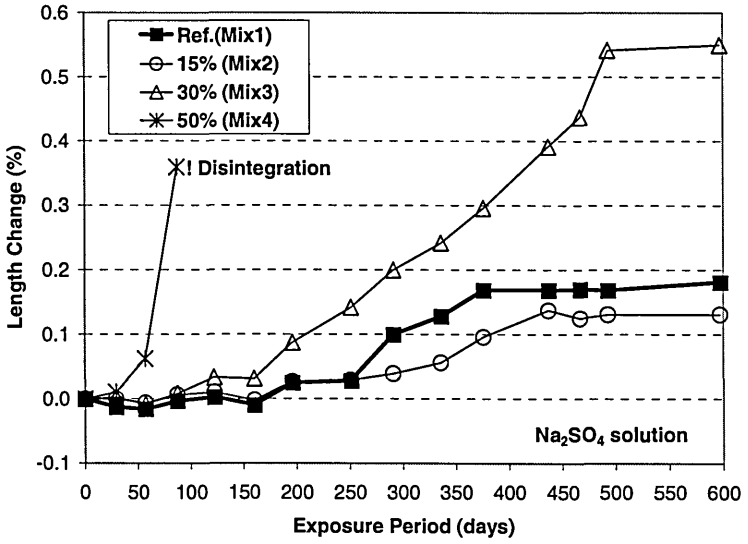


Figure 7.1. Length change of mortar specimens containing MSWI-BA (∅<212μm) as a partial replacement of cement immersed in Na_2SO_4 solution

Figure 7.2 shows the change in weight of mortar specimens containing MSWI-BA with ∅<212μm as partial replacement of cement immersed in Na_2SO_4. The replacement of cement with MSWI-BA exhibited an increase in weight when exposed to Na_2SO_4 solution. Mix 1, 2 and 3 exhibited a weight change of 3%, 4% and 5% respectively after 600 days of immersion. Contrarily, as length change indicated in Figure 7.1, Mix 2 exhibited a slightly higher weight change than Mix 1. This may indicate that Mix 2 produced more and/or heavier mass compounds than Mix 1 as a result of sulfate

exposure. However these products were accommodated in the structure without causing expansion.

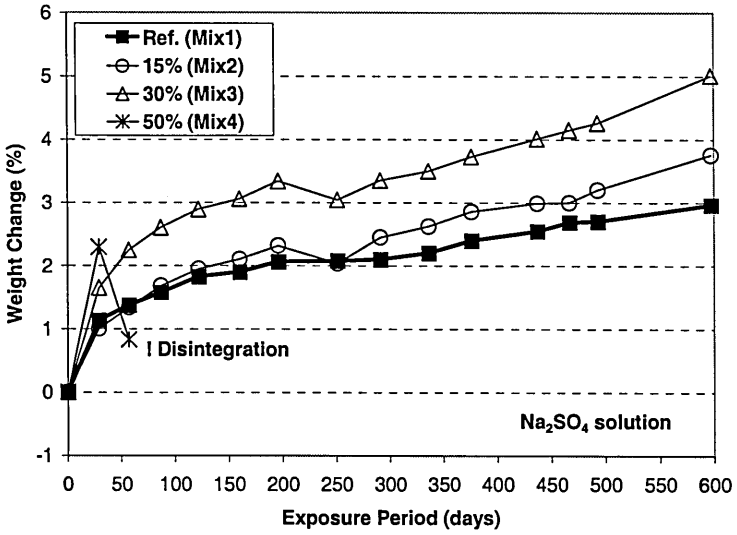


Figure 7.2. Weight change of mortar specimens containing MSWI-BA (∅<212μm) as partial replacement of cement immersed in Na_2SO_4 solution

Figure 7.3 shows the compressive strength at different ages of exposure to Na_2SO_4 solution for mortar containing MSWI-BA (∅<212μm) as a partial replacement of cement. Compressive strengths of Mix 1 and Mix 2 either increased or decreased slightly during the immersion period. The strength for both mixes was higher at 600 days of exposure than at the beginning of immersion. In other words, they did not exhibit a reduction in compressive strength as a result of sulfate immersion. The compressive strength of Mix 3 and 4 decreased significantly after approximately 200 and 50 days respectively of immersion. The overall change in strength for all mixes seemed to correlate with changes in length and weight shown in Figure 7.1 and 7.2.

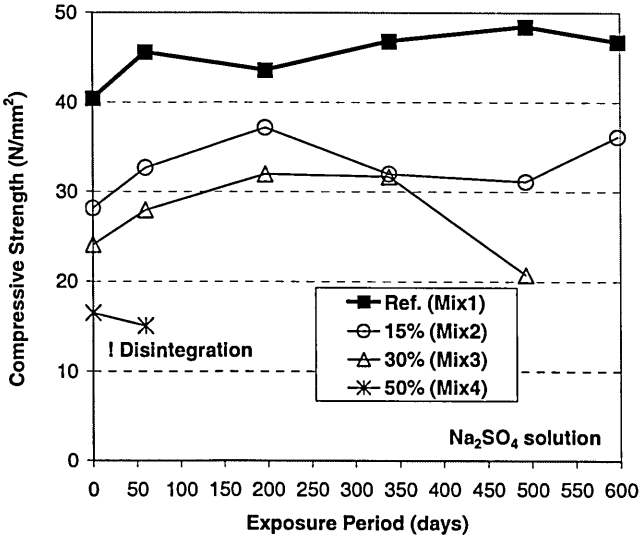


Figure 7.3. Compressive strength change of mortar containing MSWI-BA as partial replacement of cement immersed in Na_2SO_4 solution

The visual observation of the reference mix and mixes containing cement replacement levels of 15%, 30% and 50% with MSWI-BA when immersed in Na_2SO_4 is summarised in Table 7.2. In addition, photographs of theses mixes after 122 and 597 days of immersion in sulfate solution are shown in Figure 7.4.

The reference mix, mix 1, did not exhibit visual deterioration during the first year of immersion. Between one year of immersion and approximately 600 days, mix 1 showed a very slight deterioration. Mix containing 15% of cement replacement (Mix 2) exhibited the lowest degree of attack compared with the other mixes in this series. Mix 2 only exhibited very slight deterioration around the edges after 497 days of immersion. Mix containing 30% of cement replacement (Mix 3) showed very slight deterioration after 30 days of immersion. However, the deterioration increased slowly during the first year of immersion. From 376 to 597 days, Mix 3 showed moderate to severe attack. Mix containing 50% of cement replacement (Mix 4) suffered a slight attack around the edges and corners after 30 days of immersion. Mix 4 deteriorated very fast and it was totally disintegrated at 122 days.

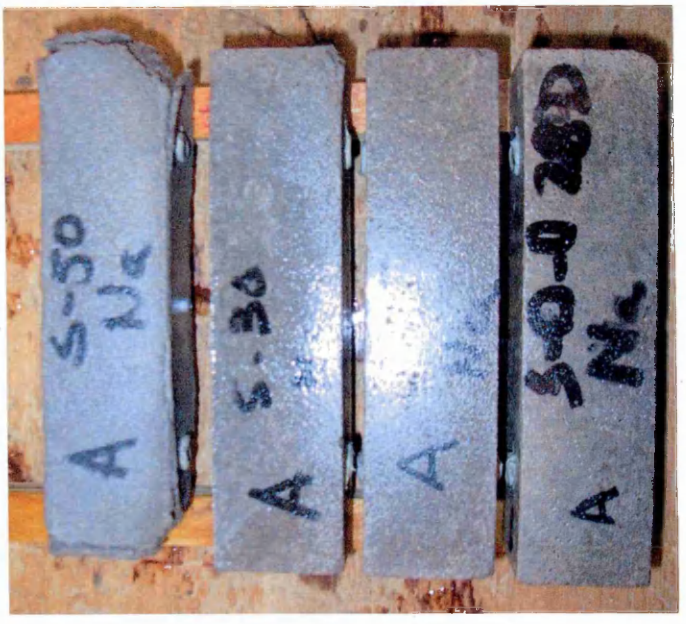
The visual observation assessment generally seemed to coincide with changes in length, weight and strength as observed in Figure 7.1, 7.2 and 7.3 respectively. The changes in length, weight, compressive strength and visual observation indicated that at 30% and 50% cement replacement levels, there was a significant decrease in sulfate resistance. However, the changes in length and visual observation indicated that 15% cement replacement exhibited slight better resistance to external sulfate attack than the reference mix whereas the changes in weight and compressive strength were slight lower for the reference.

The possible increase in sulfate resistance as a result of replacing 15% of cement with MSWI-BA may indicate a possible pozzolanic reactivity and/or better packing of MSWI-BA with $\varnothing<212\mu m$. As discussed section 7.1, pozzolanic materials (e.g. fly ash, slag) can improve the sulfate resistance of cement-based systems by consuming Portlandite and thereby decreasing the formation of gypsum (**10**). In addition, pozzolanic materials can reduce the permeability due to the refinement and block of pores. The optimum replacements of cement with pozzolanic materials to improve the sulfate resistance of cement-based systems range between 20% and 30% for fly ash and between 40% and 80% for slag (**11**). At these levels of replacement, results indicated that specimens containing MSWI-BA did not show better resistance to sulfate compared with cement-based systems containing either fly ash or slag. This suggested that MSWI-BA with $\varnothing<212\mu m$ did not behave as slag and fly ash. Chapter 9 summaries and discusses the different aspects related to possible pozzolanic reactivity of MSWI-BA with $\varnothing<212\mu m$ observed throughout this programme of research.

Table 7.2. Description of sulfate attack of mortars containing MSWI-BA (∅<212μm) as a partial replacement of cement exposed to Na_2SO_4 solution

Immersion	Ref.(Mix 1)		15% (Mix 2)		30% (Mix 3)		50%(Mix4)	
Period (days)	Description	S[a]	Description	S	Description	S	Description	S
30	No attack	0	No attack	0	Very slight attack on edges	1	Slight attack on edges and corners	2
59	No attack	0	No attack	0	Very slight attack on edges and corners	1	Moderate attack on edges and corners	3
87	No attack	0	No attack	0	Slight attack on edges and corners	2	Partial disintegration of edges, corners and faces	5
122	No attack	0	No attack	0	Slight attack on edges and corners	2	Total disintegration	6
376	Very slight attack on edges and corner	1	No attack	0	Moderate to severe attack on edges and corners	3	Total disintegration	6
493	Slight attack on edges and corners	2	Slight attack on edges	1	Moderate to severe attack on edges and corners	3	Total disintegration	6
597	Slight attack on edges and corners	2	Slight attack on edges	1	Severe attack on edges and corners	4	Total disintegration	6

[a] Numerical scale to indicate the degree of sulfate attack
0 no attack; **1** very slight attack; **2** slight attack; **3** moderate attack; **4** severe attack; **5** partial disintegration and **6** total disintegration.



(a) Mixes containing 0%, 15%, 30% and 50% as cement replacement at 87 days

(b) Mixes containing 0%, 15% and 30% as cement replacement at 597 days

Figure 7.4. Appearance of mortar specimens containing MSWI-BA (∅<212μm) as a partial replacement of cement after (a) at 87 days and (b) 597 days of immersion in Na_2SO_4 solution

7.3.2 Replacing Sand with MSWI-BA

Figure 7.5 shows the length change of mortar specimens containing 0%, 25% and 50% of MSWI-BA with 212μm<∅<2.36mm as a partial replacement of sand immersed in Na_2SO_4. The replacement of sand with MSWI-BA reduced the long–term change in length compared with the reference mix. Mixes containing 25% and 50% (Mix 5 and Mix 9) sand replacement levels exhibited slight higher length change than the reference mix during the first 250 days in sulfate solution. However, between 300 days

and 600 days, Mixes 5 and 9 exhibited lower change in length than mix 1. The reduction in length change for Mixes 5 and 9 can be associated to a possible pozzolanic reactivity and/or positive packing of particles contained in the fraction of MSWI-BA with 212μm<∅<2.36mm. These particles may contain SiO_2 that can react with $Ca(OH)_2$ thereby reducing the formation of gypsum in presence of sulfate solutions.

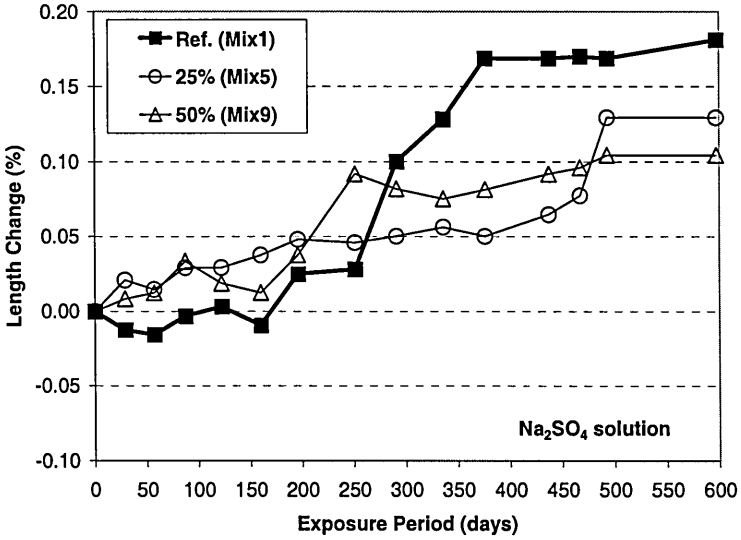


Figure 7.5. Length change of mortar specimens containing MSWI-BA (212μm<∅<2.36mm) as a partial replacement of sand immersed in Na_2SO_4 solution

Figure 7.6 shows the weight change of mortar containing 0%, 25% and 50% of MSWI-BA with 212μm<∅<2.36mm as sand replacement. The incorporation of 25% and 50% of MSWI-BA as sand replacement increased the change in weight compared with the reference mix. This increase in weight change did not coincide with the reduction in length change indicated in Figure 7.5. This effect, as discussion in section 7.3.1, is a result of the formation of compounds, likely ettringite, which are accommodated in the structure without causing expansion due to the higher pore volume compares with the reference mixes. The difference in weight change between Mix 1 and mixes containing MSWI-BA (Mix 5 and 9) was up to 0.5% at 600 days. Mix 5 and 9 exhibited similar weight change values throughout the exposure period.

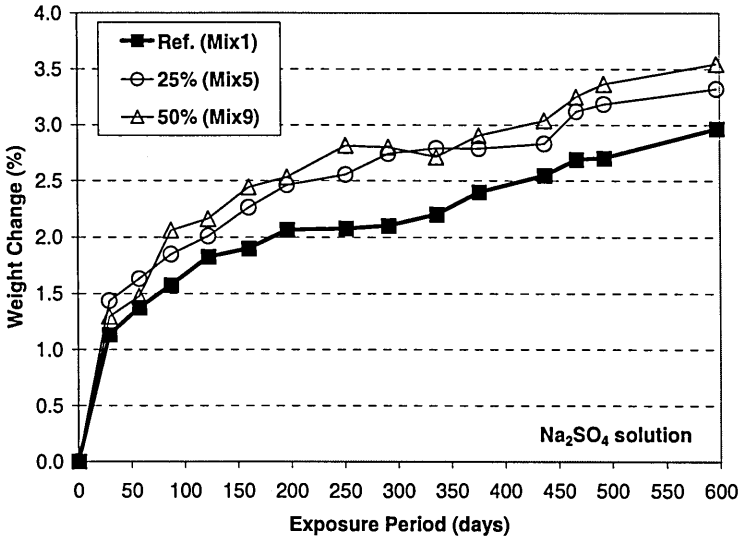


Figure 7.6. Weight change of mortar specimens containing MSWI-BA (212μm<Ø<2.36mm) as partial replacement of sand immersed in Na_2SO_4 solution

Figure 7.7 shows the compressive strength of the reference mix and mixes containing either 25% or 50% of MSWI-BA (212μm<Ø<2.36mm) as sand replacement, exposed to Na_2S0_4 solution for approximately 600 days. In general, Mix 1 exhibited a slightly higher compressive strength throughout the exposure period than mixes containing MSWI-BA (Mix 5 and 9). For Mix 5 and 9, the compressive strengths before exposure and at 600 days of immersion were similar. There was not a noticeable decrease in strength for all mixes during the exposure to sulfate solution.

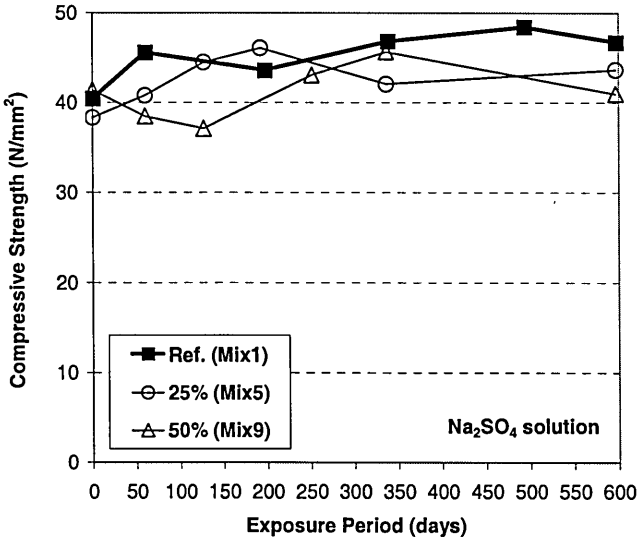


Figure 7.7. Compressive strength change of mortar specimens containing MSWI-BA (212μm<Ø<2.36mm) as a partial replacement of sand immersed in Na_2SO_4 solution

The visual observation of mixes 1, 5 and 9 exposed to Na_2SO_4 solution is summarised in Table 7.3. In addition, photographs of theses mixes after immersion at 196 and 597 days are shown in Figure 7.8. The deterioration of mix 1, has been discussed in the previous section (see section 7.3.1). In here, mix 1 was used only for comparative purposes. Mixes containing 25% and 50% of MSWI-BA as sand replacement (Mix 5 and 9) exhibited similar visual deterioration as a consequence of exposure to Na_2SO_4 solution over a period of 500 days. However, from approximately 500 days to 600 of exposure the mix containing 50% of MSWI-BA exhibited a slightly higher degree of attack. For both sand replacement levels (Mixes 5 and 9) a white layer appeared on the prism faces after a month of immersion, However, signs of attack around the edges and corners were not observed. At approximately 90 days of immersion, small cracks on some faces and very slight attack on the edges and corners of the prisms started to appear. Cracks on the faces increased in length but they did not increase in width between 87 and 196 days. At 493 days of immersion, cracks on prism faces were similar in size to those at 196 days. But at 493, moderate attack on the edges and corners were observed. For mix containing 50% of MSWI-BA, attacks on the edges and corners increased from moderate to severe at the end of the immersion period (e.g. 597 days).

The visual observation assessment of mixes containing MSWI-BA as partial replacement of sand showed higher degrees of attack than the reference mix. The visual assessment of mixes 5 and 9 did not complement the results for changes in length and compressive strength obtained in Figure 7.5 and 7.7.

Table 7.3. Description of sulfate attack of mortars containing MSWI-BA (212μm<∅<2.36mm) as a partial replacement of sand exposed to Na_2SO_4 solution

Immersion	Ref. (Mix 1)		25% (Mix 5)		50% (Mix 9)	
Period (ays)	Description	S[a]	Description	S	Description	S
30	No attack	0	Occurrence of white deposit on faces. No attack on edges or corners	1	Occurrence of white deposit on faces. No attack on edges or corners	1
87	No attack	0	Very small cracks on the middle of faces. Very slight attack on edges and corners	1	Very small cracks on the middle of faces. Very slight attack on edges and corners	1
196	No attack	0	Cracks of a few mm in length on faces. Very slight attack on edges and corners	2	Cracks of a few mm in length on faces. Very slight attack on edges and corners	2
376	Very slight attack on edges and corner	1	Slight attack on edges and corners	3	Slight attack on edges and corners	3
493	Slight attack on edges and corners	2	Moderate attack on edges and corners	3	Moderate attack on edges and corners	3
597	Slight attack on edges and corners	2	Moderate attack on edges and corners	3	Moderate to severe attack on edges and corners	4

[a] Numerical scale to indicate the degree of sulfate attack
0 no attack; **1** very slight attack; **2** slight attack; **3** moderate attack; **4** severe attack; **5** partial disintegration and **6** total disintegration.

(a) Mixes containing 25% and 50% as sand replacement at 87 days

(b) Mixes containing 25% and 50% as cement replacement at 597 days

Figure 7.8. Appearance of mortar specimens containing MSWI-BA (212μm∅<2.36mm) as a partial replacement of sand after (a) 87 days, (b) 597 days of immersion in Na_2SO_4 solution

7.3.3 Replacing Cement and Sand with MSWI-BA

Figure 7.9 shows the length change of mortar containing MSWI-BA as a partial replacement of cement and sand immersed in Na_2SO_4. Cement was replaced with 15%, 20% and 30% of MSWI-BA with ∅<212μm. Class M sand was replaced with 25% (Figure 7.9-a) and 50% (Figure 7.9-b) of MSWI-BA with 212μm<∅<2.36mm.

At 15% of cement replacement level ($C_{85\%}$-$S_{75\%}$ and $C_{85\%}$-$S_{50\%}$) the amount of MSWI-BA used as sand replacement did not influence the change in length. Therefore, mixes

$C_{85\%}$-$S_{75\%}$ and $C_{85\%}$-$S_{50\%}$ exhibited similar values in length change over the whole exposure period. Between 1 and 250 days of exposure, mixes $C_{85\%}$-$S_{75\%}$ and $C_{85\%}$-$S_{50\%}$ exhibited slightly higher length change than the reference mix (Ref. Mix 1). However, this trend changed and the change in length of mixes $C_{85\%}$-$S_{75\%}$ and $C_{85\%}$-$S_{50\%}$ were lower than of the reference mix between 250 and 600 days.

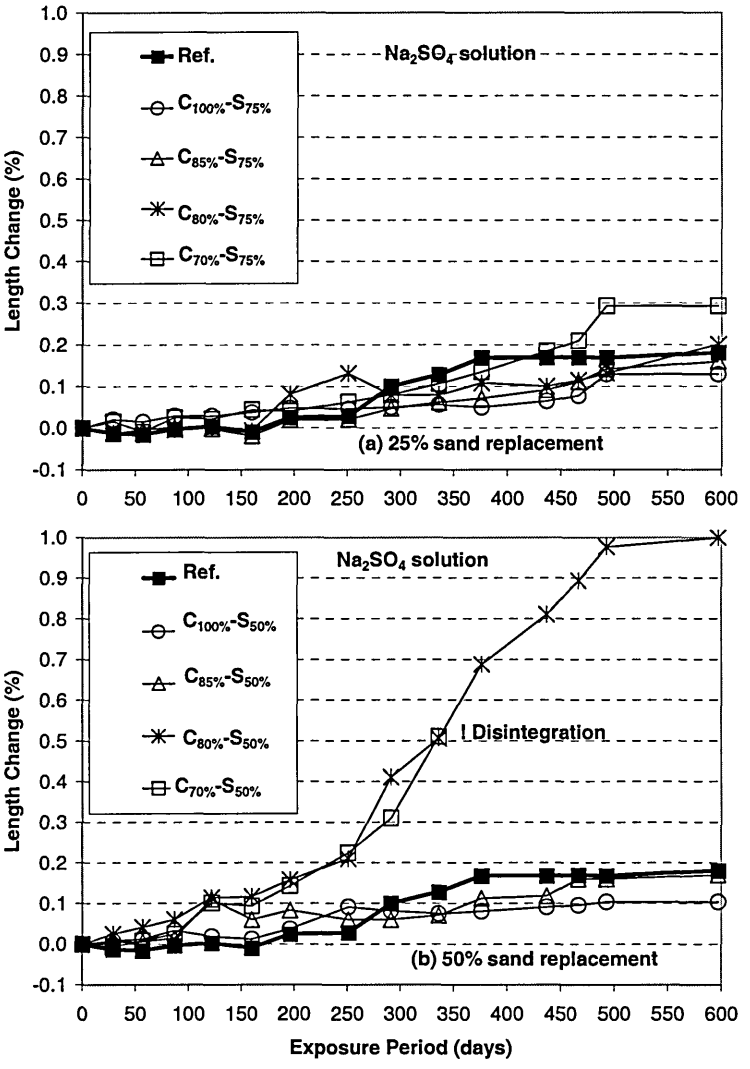


Figure 7.9. Length change of mortar containing MSWI-BA as a partial replacement of cement and at (a) 25% sand replacement and (b) 50% sand replacement immersed in Na_2SO_4 solution

At 25% (Figure 7.9-a) sand replacement length changes of mixes containing 20% and 30% of cement replacement ($C_{80\%}$-$S_{75\%}$ and $C_{70\%}$-$S_{75\%}$) were not very high compared to the reference mix. They were approximately 0.2 % and 0.3% respectively at 600 days of exposure (length change of the reference mix approximately 0.2%). However, at 50% sand replacement (Figure 7.9-b), length changes of mixes containing 20% and 30% of cement replacement ($C_{80\%}$-$S_{50\%}$ and $C_{70\%}$-$S_{50\%}$) were 0.5% after 300 days of exposure. The length change of mix $C_{70\%}$-$S_{50\%}$ could not be measured after

approximately 330 days immersed in sulfate solution as a result of the deterioration that occurred, whereas a massive length change of 1% occurs for mix $C_{80\%}$-$S_{50\%}$. The comparison of both sand replacement levels (25% and 50%) showed that at 20% and 30% cement replacement level and 50% sand replacement were significantly higher than for same cement replacement levels and 25% sand replacement.

Figure 7.10 shows the weight change of mortar containing MSWI-BA as partial replacement of cement and sand immersed in Na_2SO_4 for approximately 600 days.

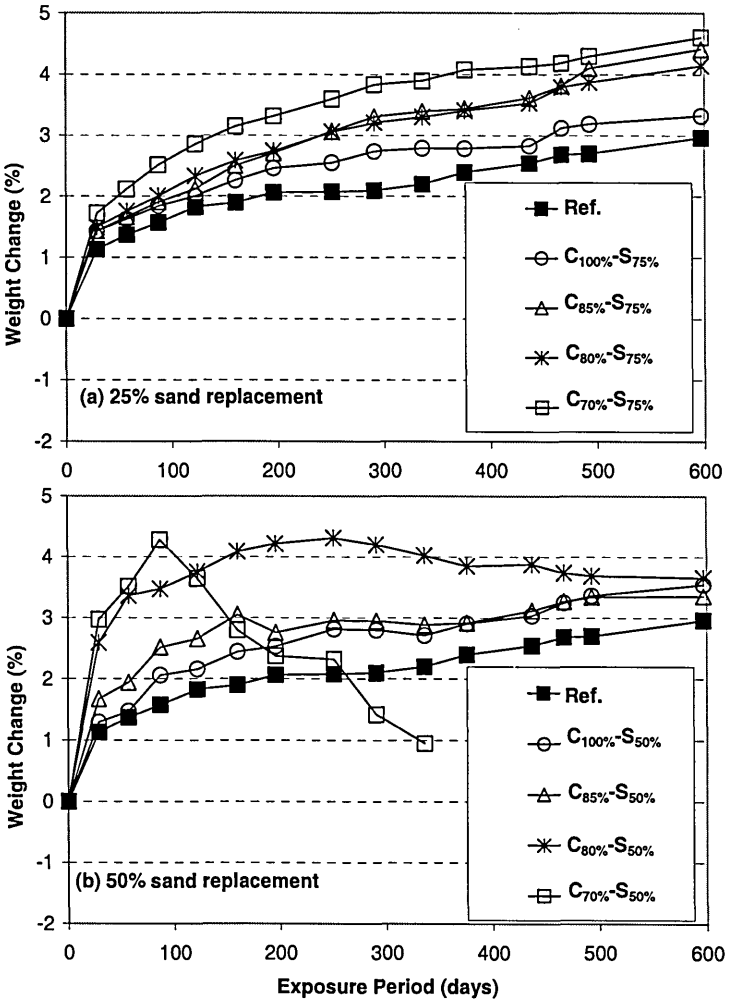


Figure 7.10. Weight change of mortar containing MSWI-BA as partial replacements of cement and at (a) 25% sand replacement and (b) 50% sand replacement immersed in Na_2SO_4 solution

In general, the incorporation of MSWI-BA with $\varnothing<212\mu m$ in binder increased the change in weight compared with the reference mix, as was found in section 7.3.1. However, the effect of replacing sand with MSWI-BA with $212\mu m<\varnothing<2.36mm$ on weight change was not always clear. The weight changes of mixes containing 25% or 50% of sand replacement levels (Mixes 5 and 9) were similar. However, weight changes of mixes containing 15%, 20% and 30% cement replacement levels and either 25% or 50% of sand replacement levels were dependent upon the sand replacement

levels. At 25% sand replacement (Figure 7.10-a), the weight changes of mixes containing 15% and 20% of cement replacement ($C_{80\%}$-$S_{75\%}$ and $C_{85\%}$-$S_{75\%}$) were similar and slightly lower than of mix containing 30% of cement replacement ($C_{70\%}$-$S_{75\%}$). At 50% sand replacement (Figure 7.10-b) the weight change of mix containing 15% cement replacement ($C_{85\%}$-$S_{50\%}$) was similar to mix $C_{100\%}$-$S_{50\%}$ (Mix 9). There was a significant increase in weight for mixes containing 20% and 30% ($C_{80\%}$-$S_{50\%}$ and $C_{70\%}$-$S_{50\%}$) after 250 days and 87 days respectively. After that, these mixes decreased in weight as a consequence of the loss of some pieces in mass caused by the severity of sulfate attack. The comparison of change in weight for mixes containing 20% or 30% cement replacement levels and either 25% or 50% coincide to observed for length change for same mixes.

Figure 7.11 shows the compressive strength of mortar containing MSWI-BA as partial replacement of cement and sand immersed in Na_2SO_4 up to approximately 600 days. In general, the incorporation of MSWI-BA as replacements of cement and sand caused changes in compressive strength throughout the exposure period. Compressive strengths of mixes containing 15% of cement replacement level and either 25% or 50% of sand replacement level were 30Nmm^{2-} before and after 597 days of exposure to sulfate solution. Compressive strength of mixes containing above 15% of cement replacement levels was dependent upon the sand replacement level used.

At 25% sand replacement (Figure 7.11–a), the mix containing 20% of cement replacement ($C_{80\%}$-$S_{75\%}$) exhibited a similar trend in strength to mix containing 15% ($C_{85\%}$-$S_{75\%}$). There was not decrease in strength for both mixes, and the strength at the end was similar to that at the beginning of the exposure. The compressive strength of mix containing 30% cement replacement ($C_{70\%}$-$S_{75\%}$) decreased after approximately 200 days of immersion.

At 50% sand replacement (Figure 7.11-b), the mixes containing 20% and 30% cement replacement ($C_{80\%}$-$S_{50\%}$ and $C_{70\%}$-$S_{50\%}$) exhibited a slight increase in strength during the first 250 days, after which the strength begun to decrease. The reduction was noticeable at high cement replacement (e.g. 30%).

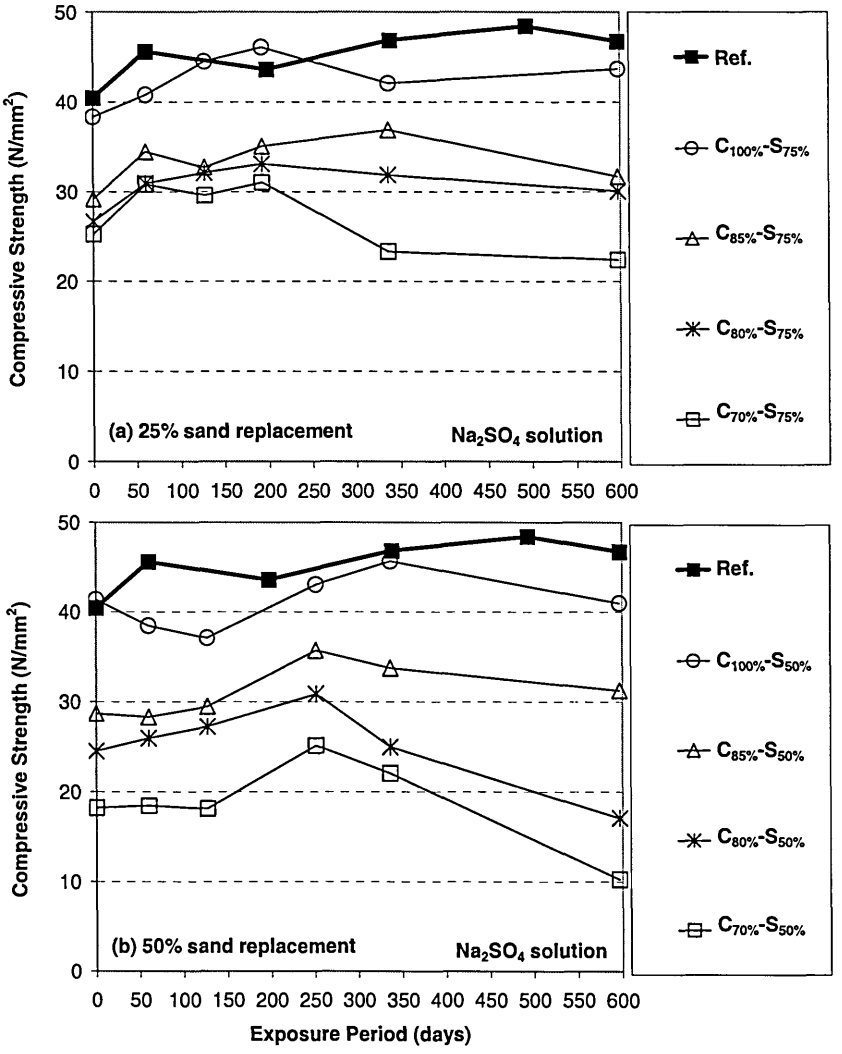


Figure 7.11. Compressive strength change of mortar containing MSWI-BA as partial replacements of cement and (a) 25% sand replacement and (b) 50% sand replacement immersed in Na_2SO_4 solution

Table 7.4 and Table 7.5 summarise the visual observations of mortar containing MSWI-BA as partial replacement of cement and sand. In addition, photographs taken at different age of immersion are shown in Figure 7.12 and 7.13 for the same mixes.

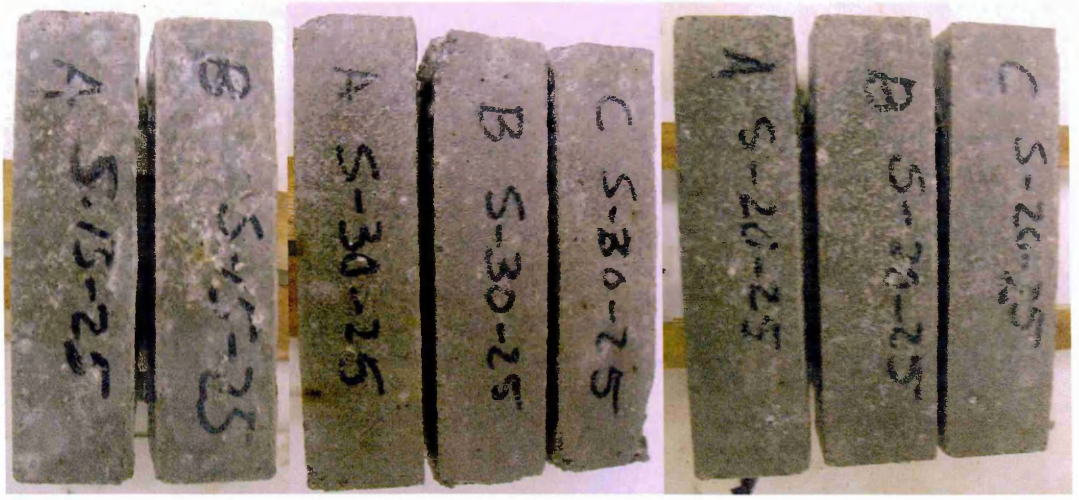
At 25% sand replacement (Table 7.4 and Figure 7.12), visual observations indicated that a white deposit appeared on the surface of all mixes after 30 days of immersion. For all mixes, very small cracks in the middle of the faces and slight attack on the edges and corners were observed after approximately 90 days. At 196 days mixes 6 ($C_{85\%}$-$S_{75\%}$) and 7($C_{80\%}$-$S_{75\%}$) exhibited similar degree of attack that observed at 90 days, whereas mix 8 ($C_{70\%}$-$S_{75\%}$) exhibited greater attack on the faces, edges and corners. At 597 days, mixes 6 and 7 exhibited moderate attack on the edges and corners whereas mix 8 showed moderate to severe attack.

Table 7.4. Description of sulfate attack of mortars containing 15%, 20%, and 30% of MSWI-BA (∅<212μm) as a replacement level of cement and 25% of MSWI-BA (212μm<∅<2.36mm) as a partial replacement of sand exposed to Na_2SO_4 solution

Immersion	$C_{85\%}$-$S_{75\%}$ (Mix 6)		$C_{80\%}$-$S_{75\%}$ (Mix 7)		$C_{70\%}$-$S_{75\%}$ (Mix 8)	
Period (Days)	Description	S	Description	S	Description	S
30	White deposit on faces. No attack on edges or corners	1	White deposit on faces. No attack on edges or corners	1	White deposit on faces. No attack on edges or corners	1
87	Very small cracks on the middle of faces. Very slight attack on edges and corners	1	Very small cracks on the middle of faces. Very slight attack on edges and corners	1	Very small cracks on the middle of faces. Very slight attack on edges and corners	1
196	Small cracks on faces. Very slight attack on faces, edges and corners	1	Small cracks on faces. Very slight attack on edges and corners	1	Cracks of a few mm in length on faces. Slight attack on edges and corners	3
376	Cracks of a few mm in length on faces. Very slight attack on faces, edges and corners	2	Small cracks of a few mm in length on faces. Very slight attack on edges and corners	2	Cracks of a few mm in length on faces. Slight attack on edges and corners	3
493	Moderate attack on edges and corners	3	Moderate attack on edges and corners	3	Moderate to severe attack on edges and corners	4
597	Moderate attack on edges and corners	3	Moderate attack on edges and corners	3	Moderate to severe attack on edges and corners	4

[a] Numerical scale to indicate the degree of sulfate attack
0 no attack; **1** very slight attack; **2** slight attack; **3** moderate attack; **4** severe attack; **5** partial disintegration and **6** total disintegration.

(a) Mixes containing 15%, 20% and 30% cement replacement levels and 25% sand replacement at 196 days



(b) Mixes containing 15%, 20% and 30% cement replacement levels and 25% sand replacement at 493 days

Figure 7.12. Appearance of mortar specimens containing 15 %, 20% and 30% replacement levels of cement and 25% replacement of sand after (a) 196 days and (b) 493 days of immersion in Na_2SO_4 solution

At 50% sand replacement (Table 7.5 and Figure 7.13), visual observations indicated that a white deposit appeared on the surface of all mixes at 30 days of immersion as found for mixes containing 25% of MSWI-BA as a partial replacement of sand. In general, the level of cement replacement influenced significantly the sulfate resistance of the mixes containing 50% MSWI-BA as a partial replacement of sand (Mix 10, 12 and 13). An increase in cement replacement caused an increase in the sulfate attack. In addition, all mixes (Mix 10, 12, and 13)) exhibited lower resistance to sulfate than those made with 25% of MSWI-BA as a sand replacement (Mix 6, 7 and 8). For example, at 196 days mixes containing 15%, 20% and 30%. Mix10 ($C_{85\%}$-$S_{50\%}$), 12 ($C_{80\%}$-$S_{50\%}$) and 13 ($C_{70\%}$-$S_{50\%}$), exhibited slight, moderate to severe and severe attack

of faces, edges and corners respectively. At 597 days, these mixes exhibited moderate, severe and total disintegration attacks respectively.

The changes in length, weight, strength and visual observation, they all coincided and indicated that mixes containing either 20% or 30% of cement replacement levels and 50% sand replacement exhibited significant lower sulfate resistance than mixes containing same cement replacement levels and 25% sand replacement.

Table 7.5. Description of sulfate attack of mortars containing 15%, 20% and 30% of MSWI-BA (Ø<212μm) as a replacement level of cement and 50% of MSWI-BA (212μm<Ø<2.36mm) as a partial replacement of sand exposed to Na_2SO_4 solution

Immersion	$C_{85\%}$-$S_{50\%}$ (Mix 10)		$C_{80\%}$-$S_{50\%}$ (Mix 12)		$C_{70\%}$-$S_{50\%}$ (Mix 13)	
Period (days)	Description	S[a]	Description	S	Description	S
30	White deposit on faces. No attack on edges or corners	1	White deposit on faces. No attack on edges or corners	1	White deposit on faces. No attack on edges or corners	1
87	Very small cracks on the middle of faces. Very slight attack on edges and corners	1	Very small cracks on the middle of faces. Very slight attack on edges and corners	1	Very small cracks on the middle of faces. Slight attack on edges and corners	2
196	Slight attack on faces, edges and corners	2	Moderate to severe attack on edges and corners.	4	Severe attack to partial disintegration of prisms.	5
376	Slight attack on faces, edges and corners	2	Moderate to severe attack on edges and corners.	4	Severe attack to partial disintegration of prisms.	5
493	Moderate attack on faces, edges and corners	3	Moderate to severe attack on edges and corners.	4	Severe attack to partial disintegration of prisms.	5
597	Moderate to severe attack on edges and corners	3 4	Severe attack to partial disintegration	5	Total disintegration	6

[a] Numerical scale to indicate the degree of sulfate attack
0 no attack; **1** very slight attack; **2** slight attack; **3** moderate attack; **4** severe attack; **5** partial disintegration and **6** total disintegration.

(a) Mixes containing 15, 20 and 30% cement replacement levels and 50% sand replacement at 196 days

(b) Mixes containing 15, 20 and 30% cement replacement levels and 50% sand replacement at 597 days

Figure 7.13. Appearance of mortar specimens containing 15%, 20% and 30% replacement levels of cement and 50% replacement of sand after (a) 196 days, (b) 597 days of immersion in Na_2SO_4 solution

7.3.3.1 Effects of Initial Curing Period and Type of Exposure on Sulfate Resistance

Figure 7.14 shows the length change for mix (Mix 10) containing 15% of MSWI-BA (∅<212μm) as replacement of cement and 50% of MSWI-BA (212μm<∅<2.36mm) as replacement of sand. Mixes were initially cured for 2, 28 and 90 days before immersion in either Na_2SO_4 or $MgSO_4$ solutions for approximately 600 days.

Figure 7.14-a shows the length change for specimens exposed to Na_2SO_4 solution. It was observed that the change in length was dependent on the curing duration prior to the immersion in the sulfate solution. Specimens subjected to an initial curing period of 90 days showed the highest change in length, followed by them cured 2 days. The

specimens initial cured for 90 days exhibited a significant increase in length after 300 days of immersion, whereas the specimens cured for 2 and 28 days showed a steady increase in length throughout the exposure period.

Figure 7.14-b shows the length change for specimens exposed to MgSO4 solution. Specimens cured for 90 days exhibited the lowest change in length up to approximately 300 days of immersion. However, after 300 days these specimens showed the highest change in length. Specimens initially cured period for 2 days and 28 days exhibited similar length change up to approximately 200 days of immersion. After 200 days, specimens cured for 28 days exhibited higher change in length than specimens cured 2 days.

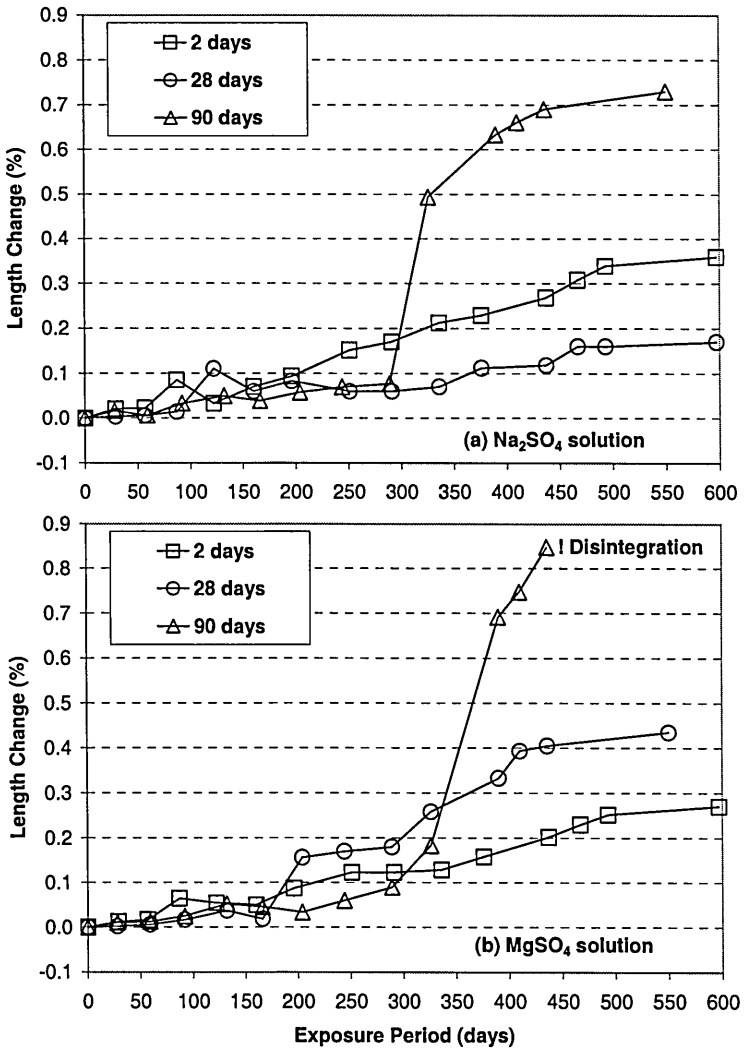


Figure 7.14. Length change of mortar specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively and initially cured for 2, 28 and 90 days before exposure to either (a) Na_2SO_4 or (b) $MgSO_4$ solutions

Specimens initially cured for 90 days showed higher increase in length change after 300 days of immersion in either Na_2SO_4 or $MgSO_4$. The increase in length change as initial curing increases was not expected. However, this trend on change in length has

also been observed with changes in weight, strength and visual assessment as shown in this section. In addition, this unexpected trend can also be correlated with the leaching behaviour of mixes initially cured for 1, 28 and 90 days before leaching (see Chapter 8).

Figure 7.15 shows the weight change for mortar containing 15% and 50% of MSWI-BA as replacement levels of cement and sand respectively, initially cured for 2 days, 28 90 days before exposure to either in Na_2SO_4 and $MgSO_4$ solutions for approximately 600 days.

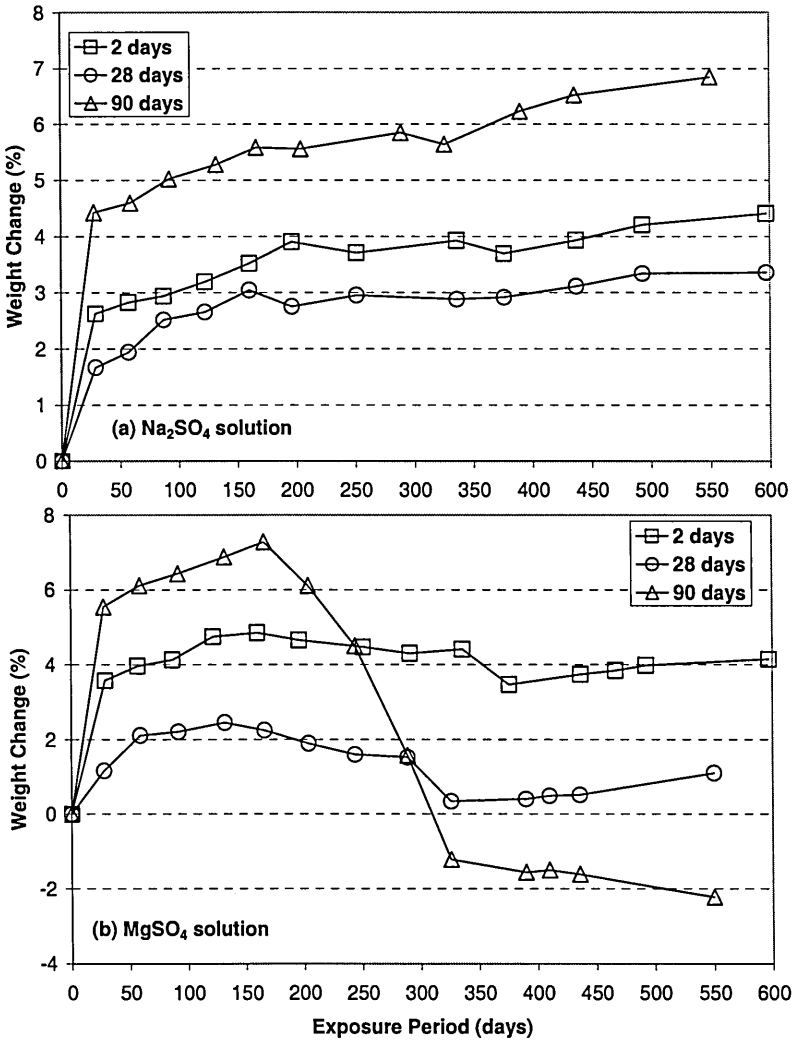


Figure 7.15. Weight change of mortar specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively and initially cured for 2, 28 and 90 days before exposure to either (a) Na_2SO_4 or (b) $MgSO_4$ solutions

Figure 7.15-a shows weight change for specimens exposed to Na_2SO_4. It suggests that the change in weight was dependent on the curing duration prior to the immersion in the sulfate solution. Specimens initially cured for 90 days showed the highest change in weight, followed by them cured for 2 days and 28 days. The mix cured for 90 days increased significantly its weight after approximately one month in sulfate exposure. All different curing periods showed an increase in weight throughout the exposure period.

Figure 7.15-b shows weight change for specimens exposed to $MgSO_4$. Specimens initially cured for 90 days exhibited a significant increase in weight up to approximately 200 days of immersion. After 200, the weight decreased drastically up to approximately 350 days due to the partial disintegration of specimens. After 350 days the weight decreased slowly. Specimens initially cured for 2 and 28 days showed similar weight change trend. There was a slight increase in weight up to approximately 150 days of immersion. After 150 days, cured periods exhibited a slow decrease up to approximately 300 days of immersion. After 300 days, the weights of specimens decreased significantly and increased up to the end of the immersion. Although both initial curing periods exhibited similar trend, specimens cured for 2 days exhibited higher values of weight change than the specimens cured for 28 days.

Figure 7.16 shows the changes in compressive strengths for mortar containing 15% and 50% of MSWI-BA as replacement levels of cement and sand respectively, and initially cured for 2, 28 and 90 days before exposure to either in Na_2SO_4 and $MgSO_4$.

Compressive strength change of mortar specimens initially cured for 90 days showed that there was a reduction in strength since beginning of the immersion in either Na_2SO_4 or $MgSO_4$ solutions. Specimens cured for 90 days and immersed in Na_2SO_4 showed a steady decrease in compressive strengths up to approximately 250 days of immersion. After 250 days the compressive strength decreased drastically. When the specimens initially cured for 90 days were immersed in $MgSO_4$, compressive strength decreased severely since the beginning of immersion.

Compressive strength of mortar specimens initially cured for 28 days before exposing to Na_2SO_4 increased and decreased slightly throughout the whole immersion. However, identical specimens immersed in $MgSO_4$ showed gradual decrease in compressive strength up to approximately 150 days of immersion. After 150 days, all cubes specimens were partially disintegrated and, therefore it was not possible to determine strength.

Compressive strength of mortar specimens initially cured for 2 days before exposing to Na_2SO_4 increased significantly during the first 30 days of immersion and kept constant up to the end of this immersion. Identical specimens immersed in $MgSO_4$ showed an

increase in compressive strength during the first months of immersion. After a month their strengths decreased slightly up to approximately 600 days of immersion.

Compressive strength of mortar specimens initially cured for 90 days decreased significantly since the beginning regardless the type of immersion used (Na_2SO_4 or $MgSO_4$), whereas compressive strengths of specimens initially cured for 2 and 28 days did not generally show this severe reduction in strength. This can be correlated with the higher changes in length and weight observed previously for specimens cured for 90 days compared with other specimens initially cured for 2 or 28 days.

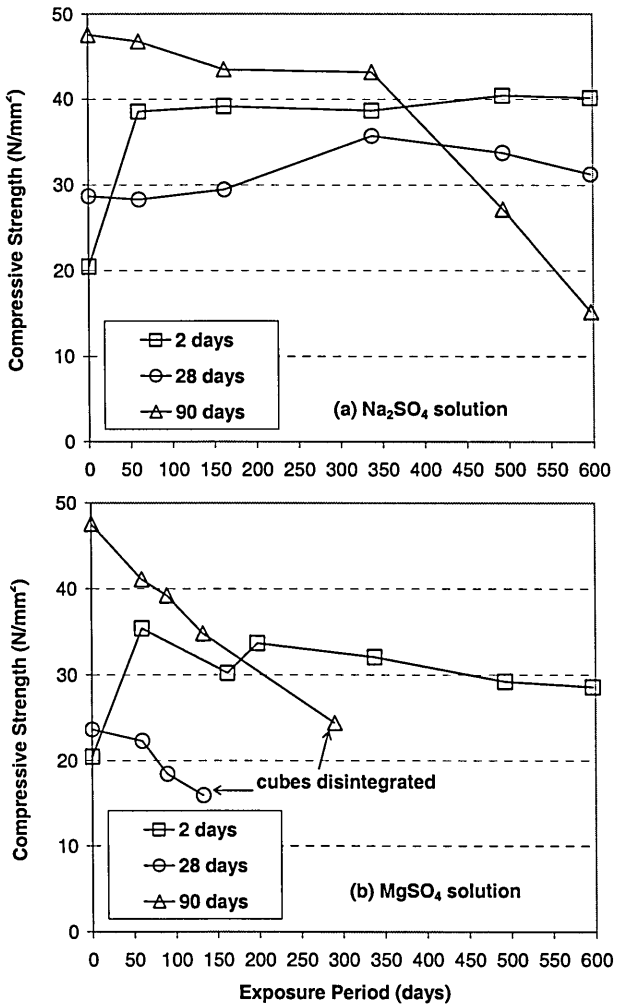


Figure 7.16. Strength change of mortar specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively and initially cured for 2, 28 and 90 days before exposure to either (a) Na_2SO_4 or (b) $MgSO_4$ solutions

Table 7.6 shows the visual observation of mortar specimens ($C_{85\%}$-$S_{50\%}$, Mix 10) containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively, and initially cured for 2, 28 and 90 days before exposure to Na_2SO_4 solution. In addition, Figure 7.17 shows the photographs of same specimens after 597 days of immersion in Na_2SO_4 solution.

Table 7.6. Description of sulfate attack of mortar containing 15% of MSWI-BA (Ø<212μm) and 50% of MSWI-BA (212μm<Ø<2.36mm) as partial replacement of cement and sand respectively, initially cured for 2, 28 and 90 days before exposing to Na_2SO_4 solution

Immersion	$C_{85\%}$-$S_{50\%}$-2 days		$C_{85\%}$-$S_{50\%}$- 28 days		$C_{85\%}$-$S_{50\%}$-90 days	
Period (Days)	Description	S[a]	Description	S	Description	S
30	White deposit on faces. No attack on edges or corners	1	White deposit on faces. No attack on edges or corners	1	White deposit on faces. No attack on edges or corners	1
87	Similar to 30 days	1	Very small cracks on the middle of faces. Very slight attack on edges and corners	1	Moderate attack on edges and corners	3
122	Slight attack on the top surface. Very slight attack on edges and corners	2	Slight attack on faces, edges and corners	2	Moderate attack on edges and corners	3
336	Moderate attack on the top surface, slight attack on edges and corners	3	Slight attack on faces, edges and corners	2	Moderate attack on edges and corners	3
493	Moderate attack on the top surface, slight attack on edges and corners	3	Moderate attack on faces, edges and corners	3	Moderate to severe attack on faces, edges and corners	3 4
597	Moderate attack on the top surface, slight attack on edges and corners	3	Moderate to severe attack on edges and corners	3 4	Severe attack on faces, edges and corners	4

[a] Numerical scale to indicate the degree of sulfate attack
0 no attack; **1** very slight attack; **2** slight attack; **3** moderate attack; **4** severe attack; **5** partial disintegration and **6** total disintegration.

In general, the visual observation of specimens initially cured for 2, 28 and 90 days and immersed in Na_2SO_4 solution coincided with changes in length, weight and strength explained previously. Thus, specimens initially cured for 90 days exhibited a moderate attack on edges and corners after 87 days of immersion whereas specimens cured for 2 and 28 days showed both similar degree of attack up to the end of immersion (597 days) to specimens cured for 90 days. Specimens cured for 90 days exhibited a severe attack at the end of the immersion. Specimens initially cured for 2 days showed

moderate attack at 336 days whereas specimens cured for 28 days exhibited moderate attack after 493 days of immersion.

Table 7.7 shows the visual observation of mortar specimens ($C_{85\%}$-$S_{50\%}$,) containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively, and initially cured for 2, 28 and 90 days before exposure to $MgSO_4$ solution. In addition, Figure 7.17 shows the photographs of same specimens after 596 days of immersion in Na_2SO_4 solution.

The visual observation of specimens initially cured for 2, 28 and 90 days and immersed in $MgSO_4$ solution can also be correlated with changes in length, weight and strength explained previously. In addition visual observation trends of specimens exposed to $MgSO_4$ solution were similar to trends showed in Na_2SO_4 immersion. However, specimens exposed to $MgSO_4$ solution exhibited higher attack than when exposed to Na_2SO_4 solution.

Results of changes in length, weight and strength and visual observation indicated that there was a reduction in sulfate resistance as initial curing period increased. This fact is not clearly explained. However, the leaching behaviour examination of identical specimens (Chapter 8) indicated similar trend. Thus, specimens initially cured for 90 days before leaching could leach out higher amount of heavy metals than specimens initially cured for 28. This common tendency for sulfate resistance and leaching behaviour may suggest that specimens cured for short periods may react with sulfate ions from the solution at early stage and form compounds (e.g. ettringite) that could decrease the later sulfate attack. This phenomenon could be associated with the improvement in sulfate resistance observed in blended materials containing C_3A in ettringite form instead of other aluminium forms (**4**).

Table 7.7. Description of sulfate attack of mortar containing 15% of MSWI-BA (∅<212μm) and 50% of MSWI-BA (212μm<∅<2.36mm) as partial replacement of cement and sand respectively, initially cured for 2, 28 and 90 days before exposing to $MgSO_4$ solution

Immersion	$C_{85\%}$-$S_{50\%}$-2 days		$C_{85\%}$-$S_{50\%}$-28 days		$C_{85\%}$-$S_{50\%}$-90 days	
Period (Days)	Description	S[a]	Description	S	Description	S
30	A layer of white deposit on faces. Top faces were swollen and soft	1	White deposit. No attack on faces, edges and corners	0	White deposit. No attack on faces, edges and corners	1
87	Moderate attack of top faces	3	Slight attack on faces, edges and corners	1	Moderate attack on edges and corners	3
122	Moderate to severe attack of the top faces. Slight attack on edges and corners	4	Moderate attack of the top faces. Slight attack on edges and corners	3	Severe attack on edges and corners	4 5
336	Severe attack on the top surface, edges and corners	4 5	Severe attack on the top surface, edges and corners	4 5	Partial disintegration	5
493	Severe attack on the top surface, edges and corners	4 5	Severe attack on the top surface, edges and corners	4 5	Partial disintegration	5
597	Severe attack on the top surface, edges and corners	5	Severe attack on the top surface, edges and corners	5	Partial disintegration	5 6

[a] Numerical scale to indicate the degree of sulfate attack
0 no attack; **1** very slight attack; **2** slight attack; **3** moderate attack; **4** severe attack; **5** partial disintegration and **6** total disintegration.

(a) Samples cured in Na_2SO_4

2 days 28 days 90 days

(b) Samples cured in $MgSO_4$

2 days 28 days 90 days

Figure 7.17. Appearance of mortar specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively. Samples initially cured for 2, 28 and 90 days, after 596 days of immersion in a) Na_2SO_4, and b) $MgSO_4$

7.3.3.2 Effect of Cement C_3A Content and Type of Exposure on Sulfate Resistance

Figure 7.18 shows the length change of mortar specimens containing 15% of MSWI-BA ($\varnothing$<212μm) as a replacement level of cement and 50% of MSWI-BA (212μm<$\varnothing$<2.36mm) as a replacement of sand. Both mixes contained similar replacement levels of MSWI-BA and were made with Portland cement with a C_3A content equal to 7.1 (Mix 10) and with a Portland cement with a C_3A content equal to 11.2 (Mix 11). Chemical compositions of both cements were provided in Chapter 3. Figure 7.18-a shows the length change for mixes 10 and 11 immersed in Na_2SO_4

whereas Figure 7.18-b shows the length change for mixes 10 and 11 immersed in $MgSO_4$ solutions for approximately 600 days.

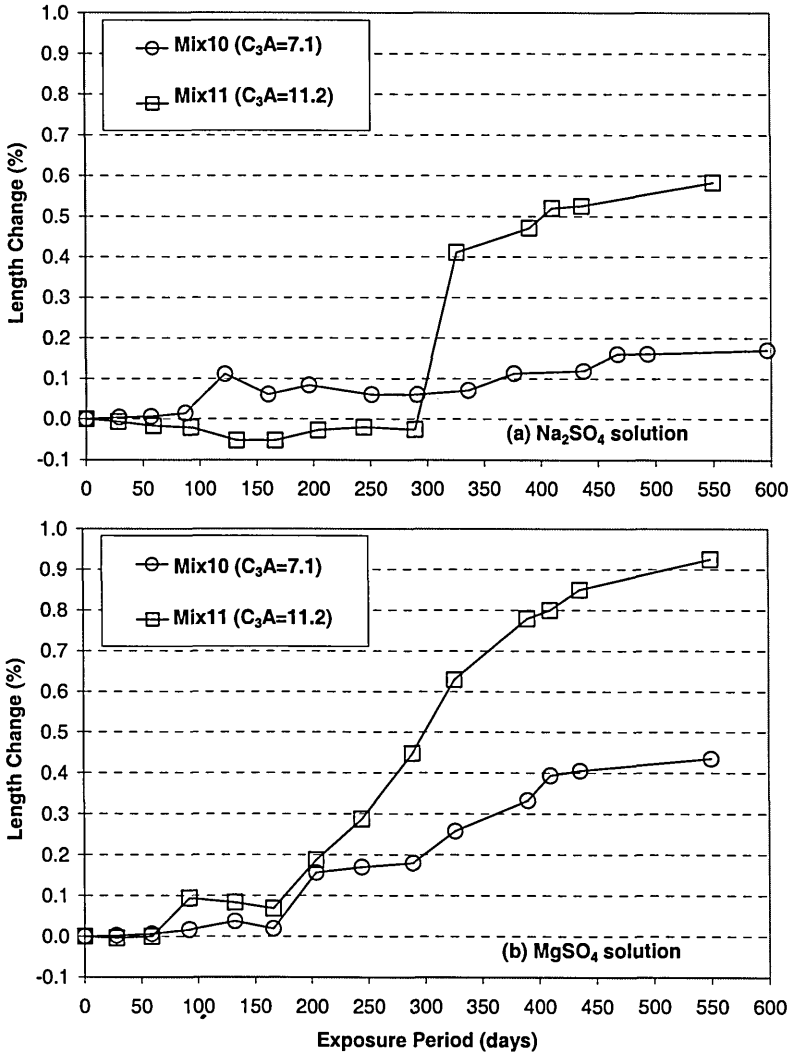


Figure 7.18. Length change of mortar specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively. Specimens made with two different cement; one with C_3A=7.1 and the other with C_3A=11.2 were immersed in either (a) Na_2SO_4 or (b) $MgSO_4$ solutions

In general, mix 11 (C_3A= 11.2) exhibited higher change in length than mix 10 (C_3A=7.1) at the end of immersion period in either Na_2SO_4 or $MgSO_4$ solution. Length mix 11 immersed in Na_2SO_4 changed very slight up to approximately 300 days of exposure. Between 300 and 350 days, the length increased drastically from 0 % to 0.4% expansion. After 350 days the length continued increasing to reach a value of approximately 0.6 to the end of the immersion. Change in length of mix 10 immersed in Na_2SO_4 was explained in section 7.3.3.

Length change of mixes 10 (C_3A=7.1) and 11 (C_3A= 11.2) exposed to $MgSO_4$ solution were similar up to approximately 250 days of immersion. After 250 days, length change of mix 11 increased drastically whereas mix 10 showed slower increase in length up to

the end of the exposure period. Length change of mixes 10 and 11 were approximately 0.4% and 0.9% at 550 days of immersion in $MgSO_4$ solution.

Figure 7.19 shows the weight change for mixes (Mix 10 and 11) containing 15% and 50% of MSWI-BA as replacement levels of cement and sand respectively, immersed in either Na_2SO_4 (Figure 7.19-a) or $MgSO_4$ (Figure 7.19-b) solution for approximately 600 days. Both mixes contained similar replacement levels of MSWI-BA were made with Portland cement with C_3A content equal to 7.1 (Mix 10) and with a Portland cement with C_3A content equal to 11.2 (Mix 11).

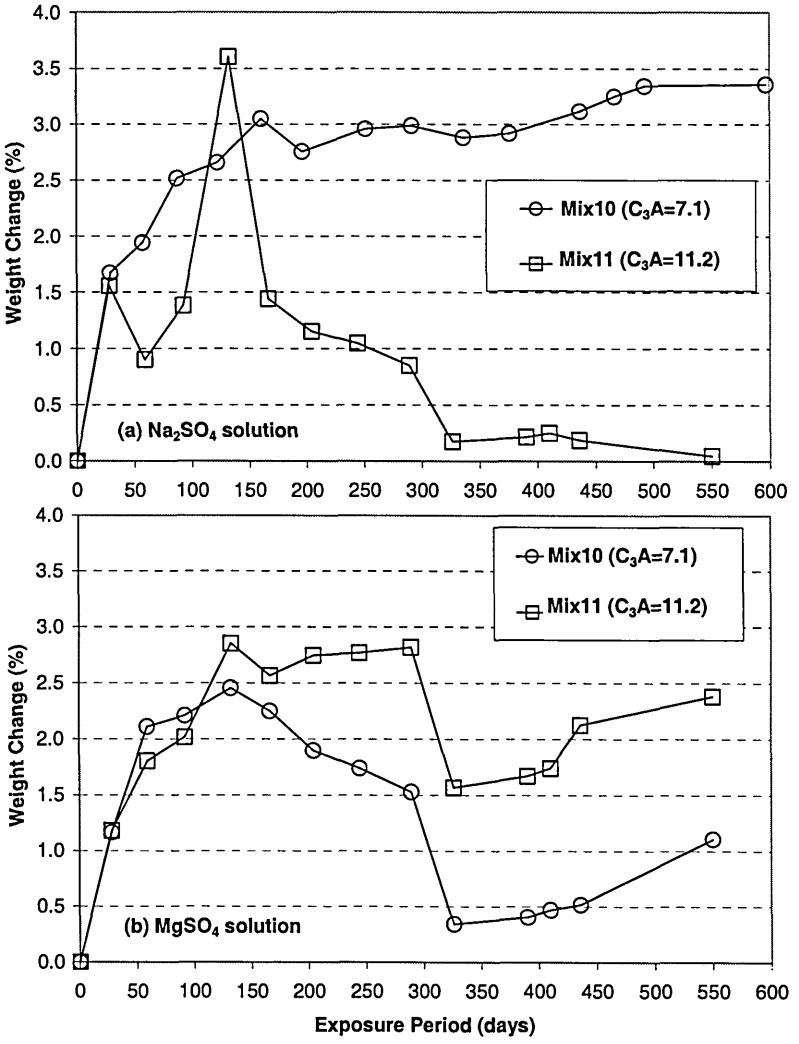


Figure 7.19. Weight change of mortar specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively. Specimens made with two different cement; one with C_3A=7.1 and the other with C_3A=11.2 were immersed in either (a) Na_2SO_4 or (b) $MgSO_4$ solutions

Mix 11 (C_3A=11.2) immersed Na_2SO_4 solution exhibited very high increase in weight between 75 days and 150 days of exposure. After 150 days the weight decreased drastically up to 325 days of immersion. This reduction in weight was due to partial disintegration of the specimens. Mix 10 (C_3A=7.1) exposed to Na_2SO_4 solution showed

a high increase in weight up to approximately 175 days of immersion . Between 175 days of immersion and the end of exposure period, the change in length of mix 10 only increased less than 0.5%.

Mixes 10 (C_3A=7.1) and 11 (C_3A=11.2) showed quite similar trend of change in weight throughout the whole $MgSO_4$ immersion period. Both mixes exhibited an increase in weight up to approximately 125 days of immersion in $MgSO_4$ solution. Between 125 days and 300 days, the weight change of mix 11 was approximately constant whereas mix 10 exhibited a notable decrease in weight. Between 300 and 325 days, both mixes showed a significant decrease in weight. After 325 days, Mix 10 and 11 exhibited an increase in weight change up to the end of exposure period

Compressive strength of mortar specimens made with a Portland cement with C_3A content equal to 11.2 (Mix 11) was not monitored as it was for specimens made with Portland cement with C_3A content equal to 7.1 (Mix 10). Thus, the comparison of compressive strength changes between mixes 10 and 11 was not possible.

Table 7.8 and Table 7.9 show the visual observations of for mixes 10 (C_3A=7.1) and 11 (C_3A=11.2) exposed to Na_2SO_4 and $MgSO_4$ solutions for approximately 600 days. Both mixes contained 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively.

Prisms of mixes 10 and 11 immersed in Na_2SO_4 solution showed a clear difference in rate and degree of sulfate attack along the exposure period. Mix 11 containing high C_3A (C_3A=11.2) cement started to deteriorate earlier and showed higher deterioration after approximately 600 days of immersion than mix 10 made with lower C_3A content (C3A=7.1) cement. Mix 11 was partially disintegrated at approximately 200 days of immersion whereas mix 10 exhibited slight attack on faces, edges and corners at approximately 375 days of immersion. The increase in sulfate attack for the mix containing high C_3A cement was due to the increase in C-A-H products that enhanced the formation of ettringite as a result of sulfate attack (**10**). This was discussed in detail in Chapter 2.

Prisms of mix 10 and 11 immersed in MgSO4 solution exhibited similar degree and rate of sulfate attack along the exposure period. This was in agreement with Santhanam et al results (**1**), which suggested that the use of low C_3A cement may be not adequate when specimens were exposed to $MgSO_4$ solution. The decrease of C-A-H products may facilitate the direct attack of C-S-H products.

In addition it was observed that specimens containing high C_3A cement (Mix 11) exhibited a similar degree of sulfate attack at approximately 600 days of exposure regardless of type of immersion used.

Table 7.8. Description of sulfate attack of mortars containing 15% of MSWI-BA (∅<212μm) and 50% of MSWI-BA (212μm<∅<2.36mm) as a partial replacement of cement and sand respectively made with two Portland cements; one with a C_3A=7.1 (Mix 10)and the other with C_3A=11.2 (Mix 11). Specimens were exposed to Na_2SO_4 solution

Immersion	Mix 10 (C_3A=7.1))		Mix 11 (C_3A=11.2)	
Period (days)	Description	S[a]	Description	S
30	White deposit on faces. No attack on edges or corners	1	White deposit on faces. No attack on edges or corners	1
87	Very small cracks on the middle of faces. Slight attack on edges and corners	2	Moderate attack on corners	3
196	Slight attack on faces, edges and corners	2	Severe attack on corners. Loss of mass from corners	4 5
376	Slight attack on faces, edges and corners	2	Partial disintegration of corners	5
493	Moderate attack on faces, edges and corners	3	Partial disintegration of corners. Attack on top face	5 6
597	Moderate to severe attack on edges and corners	3 4	Partial disintegration of corners. Attack on top face	5 6

[a] Numerical scale to indicate the degree of sulfate attack
0 no attack; **1** very slight attack; **2** slight attack; **3** moderate attack; **4** severe attack; **5** partial disintegration and **6** total disintegration.

Table 7.9 . Description of sulfate attack of mortars containing 15% of MSWI-BA (Ø<212μm) and 50% of MSWI-BA (212μm<Ø<2.36mm) as a partial replacement of cement and sand respectively made with two Portland cements; one with a C_3A=7.1 (Mix 10) and the other with C_3A=11.2 (Mix 11). Specimens were exposed to $MgSO_4$ solution

Immersion Period (days)	Mix 10 (C_3A=7.1)) Description	S[a]	Mix 11 (C_3A=11.2) Description	S
30	White deposit. No attack on faces, edges and corners	0	A layer of white deposit on faces. Very slight attack on faces edges and corners	1
87	Slight attack on faces, edges and corners	2	Slight attack on faces, edges and corners	2
122	Moderate attack of the top faces. Slight attack on edges and corners	3	Moderate attack on edges and corners. Mortar looked soft and lack of bond between concrete constituents	3
336	Severe attack on the top surface, edges and corners	4 5	Severe attack on the top surface, edges and corners	4 5
493	Severe attack on the top surface, edges and corners	4 5	Severe attack on the top surface, edges and corners	4 5
597	Severe attack on the top surface, edges and corners to partial disintegration	5 6	Severe attack on the top surface, edges and corners to partial disintegration	5 6

[a] Numerical scale to indicate the degree of sulfate attack
0 no attack; **1** very slight attack; **2** slight attack; **3** moderate attack; **4** severe attack; **5** partial disintegration and **6** total disintegration.

Figure 7.20 and Figure 7.21 show the photographs of prisms containing low C_3A content cement (mix 10) and prisms containing high C_3A content cement (mix 11) immersed in either Na_2SO_4 and Mg SO_4 solutions at 87 and 493 of immersion.

(a) High C_3A Cement (11.2%)

$MgSO_4$ Na_2SO_4

(b) Low C_3A Cement (7.1%)

$MgSO_4$ Na_2SO_4

Figure 7.20. Appearance of mortars containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively. Two Portland cements were used, one with a) 11.2% C_3A content and b) 7.1% C_3A content. Samples were exposed to $MgSO_4$ and Na_2SO_4 for 87 days

(a) High C_3A Cement (11.2%)

$MgSO_4$ Na_2SO_4

(b) Low C_3A Cement (7.1%)

$MgSO_4$ Na_2SO_4

Figure 7.21. Appearance of mortars containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively. Two Portland cements were used, one with a) 11.2% C_3A content and b) 7.1% C_3A content. Samples were exposed to $MgSO_4$ and Na_2SO_4 for 493 days

7.4 CONCLUSIONS

This chapter has examined the sulfate resistance of mixes containing MWSI-BA as partial replacement of cement and/or sand exposed to Na_2SO_4. In addition, the effects of using two sulfate solutions (i.e. Na_2SO_4 and $MgSO_4$), three initial curing periods (i.e. 2, 28 and 90 days) and two cements with different C_3A contents (C_3A=7.1 and C_3A=11.2) on the sulfate resistance have been evaluated for mixes containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively. Sulfate attacks on mortar specimens were evaluated measuring changes in weight, length and compressive strength and observing visual deteriorations.

Conclusions of sulfate resistance for mortar specimens are presented in the following items:

1. Effect of replacing 15%, 30% and 50% of cement with MSWI-BA with $\varnothing$<212μm.
2. Effect of replacing 25% and 50% of sand with MSWI-BA with 212μm <$\varnothing$<2.36mm.
3. Effect of replacing cement and sand with MSWI-BA with $\varnothing$<212μm and 212μm<$\varnothing$<2.36mm respectively.
4. Influence of type of sulfate solution, initial curing period and cement C_3A content for specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively.

Replacing cement with 15% of MSWI-BA with $\varnothing$<212μm caused a slight reduction in the sulfate attack caused by exposing to Na_2SO_4 solution compared with the sulfate attack observed for the reference mix. However, cement replacement levels of 30% and 50% caused a significant decrease in the sulfate resistance of specimens containing MSWI-BA.

The appearance of specimens containing 25% and 50% of MSWI-BA 212μm<$\varnothing$<2.36mm as a partial replacement of sand indicated a higher degree of sulfate attack compared with the reference mix specimens. However, changes in length and strength of specimens containing MSWI-BA were similar to those for the reference mix. Specimens containing 50% of MSWI-BA as a partial replacement of sand showed a slightly higher degree of attack than those containing 25% replacement levels. All specimens containing MSWI-BA presented a white deposit on their faces after a month exposed to Na_2SO_4 solution, which lead to further cracking. This may be attributed to occurrence of alkali-silica reaction due to presence of silica in the MSWI-BA used as partial replacement of sand and the excess of Na^+ ions from the sulfate solution.

Replacing cement and sand with MSWI-BA generally increased the degree of sulfate attack as replacement levels increased. However, there are some exceptions. At 20% and 30% cement replacement levels, specimens containing 50% as partial

replacement of sand exhibited significantly higher sulfate attack than specimens containing 25% as a partial replacement of sand, whereas specimens containing 15% and 50% cement and sand replacement levels respectively exhibited similar or slightly higher sulfate attack than those containing 25% of sand replacement at same cement replacement level. Sulfate resistance of specimens containing 15% of MSWI-BA as a partial replacement of cement and either 25% or 50% as a partial replacement of sand was similar to that for specimens containing 100% cement in the binders.

The evaluation of the influence of initial curing period on sulfate resistance of specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively showed a slight decrease in sulfate resistance as initial curing period increased. This was not expected, however, further examination of leaching behaviour for same mixes (Chapter 8) indicated the same trend. This may be attributed to the formation of ettringite at early plastic stage that can be accommodated without disrupting the structure due to the high pore volume of mixes containing MSWI-BA as replacement of cement and sand. Specimens cured initially for short period prior may form ettringite by combination of C_3A with the sulfate ions rather than other aluminate monosulfates, which are formed when there are not enough sulfate ions to form ettringite. In addition, it was observed that $MgSO_4$ exposure caused higher deterioration of specimens than Na_2SO_4 exposure for all different initial curing period examined. The examination of cement C_3A content effect on sulfate resistance has shown different behaviours of cements depending on the type of immersion used. Hence, in $MgSO_4$ immersion cement with low (7.1) and high (11.2) C_3A contents exhibited similar deterioration rate and degree of attack. These specimens looked soft and lack of bond between concrete constituents. The sulfate resistance of specimens immersed in Na_2SO_4 solution was dependent on cement C_3A content. Specimens made with high C_3A cement showed higher deterioration rate and sulfate attack than those made with low C_3A cement. The degree of sulfate attack for specimens made with the cement C3A=11.2 and immersed in Na_2SO_4 solution was similar to specimens immersed in $MgSO_4$ solution. However, the specimens immersed in Na_2SO_4 had higher deterioration rate than those immersed in $MgSO_4$ and different appearance. The firmer specimens (Na_2SO_4) lost part of mass from corners and edges but they looked hard whereas the later ($MgSO_4$) looked soft. This difference in sulfate attacks can be attributed to high ettringite formation due to the high C_3A content for specimens immersed in Na_2SO_4 solution and the formation of gypsum as a result of reaction of C-S-H with $MgSO_4$ solution.

In order to extent and continue the study on MSWI-BA contained in mortars, next chapter, Chapter 8 will examine the leaching behaviour of mortar containing MSWI-BA as partial replacement of cement and sand.

7.5 REFERENCES

1 Santhanam M., Cohen M.D., Olek J. "Sulfate Attack Research - Whither Now?". Cement and Concrete Research, Vol. 31, pp.845-851. 2001

2 Brown P.W. and Badger S. "The Distributions of Bound Sulfates and Chlorides in Concrete Subjected to Mixed NaCl, $MgSO_4$, Na_2SO_4 Attack". Cement and Concrete Research, Vol 30, pp 1535-1542. 2000

3 Santhanam M., Cohen M.D. and Olek J. "Mechanism of Sulfate attack: A fresh look Part 1: Summary of Experimental Results". Cement and Concrete Research Vol. 32 pp 915-921. 2002

4 O'Farrell M. Wild S. Sabir B.B. "Resistance to Chemical Attack of Ground Brick-PC Mortar. Part: Sodium Sulfate Solution". Cement and Concrete Research Vol. 29 pp 1781-1790. 1999

5 Thomass M.D.A., Shehata M.H., Shashiprakash S.G. and Hopkins D.S. "The Use of Ternary Cementitiuos Systems Containing Silica Fume and Fly Ash in Concrete". Cement and Concrete Research Vol. 29 pp 1207-1214. 1999

6 Osborne G.J. "Durability of Portland Blast-Furnace Slag Cement Concrete". Cement and Concrete Composites. Vol. 21, pp 11-21. 1999

7 BS 12. 1996: Specification for Portland cement

8 BS 882:1992. Specifications for Aggregates from Natural Sources for Concrete

9 Barker A.P. and Hobbs D.W. "Performance of Portland Limestone Cements in Mortar Prisms Immersed in Sulfate Solutions at 5°C". Cement and Concrete Composites Vol. 21 pp 129-137. 1999

10 Santhanam M., Cohen M.D. and Olek J. "Effect of Gypsum Formation on the Performance of Cement Mortars during External Sulfate Attack". Cement and Concrete Research, Vol. 33, pp. 325-332. 2003

11 Wright L. PhD Thesis "Properties of Concrete Containing Desulphurised Waste". Sheffield Hallam University. 2003

CHAPTER 8: LEACHING BEHAVIOUR OF MORTAR CONTAINING MSWI-BA

8.1 INTRODUCTION

The use of wastes in construction that may contain hazardous elements or compounds, requires the assessment of their impact on the environment. Thus, the environmental quality of cement-based systems containing potential or relatively new wastes is as important aspect as it is the examination of the engineering properties. The environmental impact of these systems on the environment can be assessed by examining the long-tern leaching behaviour of toxic compounds (i.e. heavy metals, sulfates and chlorides) (**1**,**2**). In addition, the examination of leaching behaviour can provide information about the physical and chemical interactions between the waste particles and the cement and aggregates (**3**).

Leaching tests have been developed to evaluate the different aspects of leaching, throughout the world (**3**,**4**). For monolithic materials (e.g. concrete or mortar), tank tests are to be considered the most suitable tests for assessing the long-term leaching behaviour. However, most of the published studies on leaching behaviour of cement-based systems containing waste have used other tests such as bath or column procedures. The tank leaching tests are dependent on the experimental parameters used for the procedure. This includes liquid/solid (l/s) ratio, leachant type, test duration and number of leachant removals (**5**).

There is not yet a European tank leaching procedure to evaluate the leaching of concrete (**6**). Nevertheless, most of the published work on leaching of cement-based systems either with or without the presence of waste material has used the experimental parameters in accordance with NEN 7345 tank leaching procedure (**7**) The NEN 7345 is a rapid and inexpensive procedure to examine long-term leaching. The access of CO_2 is not controlled during the test and this can cause a variable extend of carbonation of the cube faces (**4**). However, the variation of carbonation does not have a significant influence on leaching results (**4**,**6**).

At present, the long-term leaching behaviour of concrete containing MSWI-BA is still in the early stage and not published widely in the literature (**8**,**9**). Hence, this chapter examines the long-term leaching behaviour of metals, sulfates and chlorides from mortar containing MSWI-BA. Leachability of the mortar specimens is examined using a tank leaching procedure. Since there is not a well-established standard leaching procedure for mortar or concrete specimens, different experimental leaching parameters were tested. In addition, leaching behaviour of mortars containing various MSWI-BA replacement levels was examined to identify the difference in leaching when MSWI-BA was used as partial replacement of cement or sand.

8.2 EXPERIMENTATION

8.2.1 Materials

The materials that were used in this chapter were MSWI-BA with particle diameter (∅) below 212μm and a standard 42.5 Ordinary Portland Cement conforming to BS12: 1996 (**10**), MSWI-BA with 212μm<∅<2.36mm and class M sand according to BS 882:1992 (**11**). The oxide contents for cement, class M sand and MSWI-BA, as well as their physical properties are provided in Chapter 3 and Chapter 4.

In addition of constituents of cement-based systems, reagents such as deionised water, standard solutions for ICP-OES and ICP-MS were used (see Chapter 3).

The rain water that was used for one leaching test was collected from rainfall during one month and stored for a few weeks before leaching test took place. During the storage period, its pH was monitored. The pH was kept constant, around 5.5, after a few days from the collection.

8.2.2 Mix Proportion

The proportion of binder to aggregate (b:a) was 1:3 and water/binder (w/b) ratio was 0.50. Binders included the standard 42.5N cement and MSWI-BA with ∅<212μm. Cement was uniquely replaced by 15% of MSWI-BA. Aggregates consisted of the class M sand with ∅<2.36mm and MSWI-BA with 212μm<∅<2.36mm. The sand was replaced with 50%.

The preparation of mixes, which involves mixing, casting and curing, was explained in Chapter 3.

8.2.3 Testing

8.2.3.1 Tanks Leaching Procedure

The leaching was examined using cube specimens of 50mm in size. These cubes were stored in mist room at 20°C and 97%±3 RH after de-moulding until leaching test took place.

Leaching performance of mortar mixes was assessed using a tank leaching test, which adopted the characteristic of the leaching protocol developed by Groot et al (**6**). Groot et al. protocol is based on the principles of the Dutch NEN 7345 tank leaching test. In this test, leaching of components from the mortar specimens is determined by submersing the specimen in de-mineralised water and renewing the leachates at 5 fixed times.

For all leaching series conducted, the common experimental parameters were:

a) duration of procedure was 14 days,

b) leachant was renewed at 6 hours, 24 hours, 3 days, 7 days and 14 days,

c) volume of leachant was 850ml,

d) specimens were cubes of 50mm in size,

e) there was no agitation

f) test were carried out at 20±5ºC.

Figure 8.1 shows a sketch of leaching tank procedure. Mortar specimens were placed in a closed tank and filled with 850 ml of leachant. Cube specimens were placed in the middle of the tanks and supported so as to allow direct contact between all cube faces and the leachants. Tank tests were covered and specimens were in contact with air only during leachant renewal.

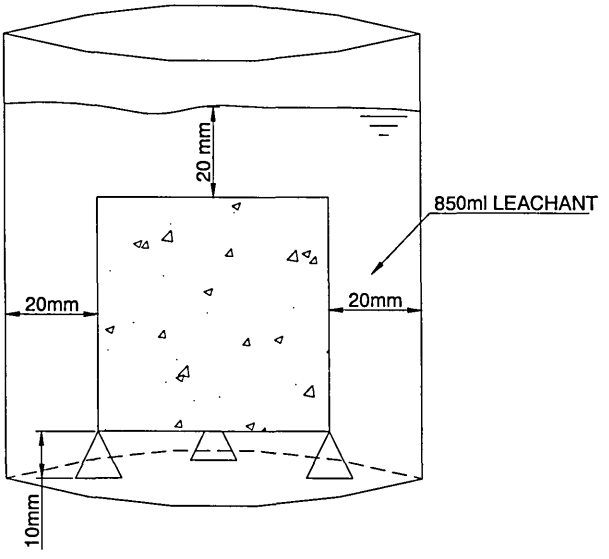


Figure 8.1. Sketch of the leaching tank test used

Leachates were removed at 6h, 24h, 3, 7 and 14 days. The removed leachates were passed through vacuum filtration using a 0.45μm glass fibre filter. After filtration, leachates used for the determination of metals were acidified to pH=2 using HNO_3. Addition of acid was required to avoid precipitation of some metals (**12**). Leachates used for the determination of sulfates and chlorides were stored without adding acid. The determination of SO_4^{2-} and Cl^{1-} was carried out a few days after leachates were obtained because leachates had not been acidified whereas the determination of metals was carried out within a month from extraction of the leachates.

Four experimental series, L1, L2, L3 and L4, were conducted to examine the leaching behaviour of mortar containing MSWI-BA. The mix proportion used for series L1, L2 and L3 is shown in Table 8.1.

Table 8.1. Mix proportion used for leaching series L1, L2 and L3

Series ID	binder		Aggregate	
	Cement	MSWI-BA Ø<212μm	Sand	MSWI-BA 212μm<Ø<2.36mm
L1	85%	15%	50%	50%
L2	85%	15%	50%	50%
L3	85%	15%	50%	50%

The experimental parameters (i.e. tests duration, leachant removal, specimen size, temperature, no agitation, filtration and storage) were the same for all experimental series.

Details of the experimental series are follows;

1. **Series 1**: *Influence of initial curing.* This series, L1, examined the effect of initial curing period on leachate concentrations. The three curing periods considered were 1 and 90 days. Table 8.2 shows experimental parameters using for this series. Leachants consisted of de-ionised water acidified with HNO_3 to achieve a pH of approximately 2. In addition, a few drops of HNO_3 were added 5 times during the test, in order to keep the pH around 4.

Table 8.2. Leaching procedure details for leaching series L1

ID	Initial Curing	Leaching procedure	
		Leachant[a]	Acid addition[b]
pH_{ac}(1d)	1 day	pH≤2	Yes
pH_{ac}(90d)	90 days	pH≤2	Yes

a- leachant pH before contact with the specimens

b- addition of HNO_3 to keep the pH between 2 and 4 during the leaching test

2. **Series 2**: *Effect of adding acid.* This series, L2, was carried out to compare the difference in leachate concentrations between two leaching procedures; one procedure involved the addition of a few drops of HNO_3 during the test, as described in series L1; the other procedure was conducted without adding acid. Both procedures used same leachants that consisted of de-ionised water acidified with HNO_3 to achieve a pH of approximately 2. The influence of acid addition was examined for mixes with an initial curing period 90 days. Table 8.3 leaching procedure details for leaching series L2.

Table 8.3. Leaching procedure details for leaching series L2

	ID	Initial Curing	Leaching procedure	
			Leachant[a]	Acid addition[b]
Procedures 1	**pH_{ac}(90d)**	90 days	pH≤2	Yes
Procedures 2	**pH(90d)**	90 days	pH≤2	No

a- leachant pH before contact with the specimens

b- addition of HNO_3 to keep the pH between 2 and 4 during the leaching test

3. **Series 3**: *Leachant type influence*. Series L3 examined the effect of using three different leachants on leachate concentrations. The leachants were rain water, de-ionised water and of de-ionised water acidified with HNO_3 to achieve a pH of approximately 2. Table 8.4 shows the leaching procedure details for this series. Initial curing period for all specimens of this series was 28 days and HNO3 was not added during the test.

Table 8.4. Leaching procedure details for leaching series L3

ID	Initial Curing	Leaching procedure	
		Leachant	Acid addition[b]
pH(28d)	28 days	pH≤2[a]	No
Ion(28d)	28 days	De-ionised	No
Rain(28d)	28 days	Rain water	No

a- leachant pH before contact with the specimens

b- addition of HNO3 to keep the pH between 2 and 4 during the leaching procedure

4. **Series 4**: *Effect of the type of MSWI-BA replacement*. This series examined the difference in leaching behaviour of mortar specimens containing MSWI-BA as a replacement of either cement or sand. Table 8.5 provides the mixes proportion of different mixes used and the leaching procedure characteristics. Three mixes were prepared. Mix 1 contained 15% of MSWI-BA with ∅<212μm as replacement of cement and 50% of MSWI-BA with 212μm<∅<2.36mm as replacement of sand. Mix 2 contained 50% MSWI-BA with 212μm<∅<2.36mm as replacement of sand and mix 3 consisted of a reference mix.

Table 8.5. Mix and leaching procedure details for leaching series L4

Mix Number	ID	Mix design				Leaching procedure		
		Cement	MSWI-BA Fine[1]	Sand	MSWI-BA Coarse[2]	Curing Period	Leachant[a]	Acid Addition[b]
1	$C_{85\%}$-$S_{50\%}$	85%	15%	50%	50%	28 days	pH≤2	No
2	$C_{100\%}$-$S_{50\%}$	100%	0%	50%	50%	28 days	pH≤2	No
3	$C_{100\%}$-$S_{100\%}$	100%	0%	100%	0%	28 days	pH≤2	No

1- MSWI-BA with Ø<212μm 2- MSWI-BA with 212μm<Ø<2.36mm

a- leachant pH before contact with the specimens

b- addition of HNO3 to keep the pH between 2 and 4 during the leaching test

8.2.3.2 Determination of Elements

Leachate concentrations for 22 metal elements were determined. Concentrations of Ca, Si, Al, Mg, Fe, K and Na were measured using ICP-OES technique, whereas the concentrations of B, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Sn, Cd, Ba, Hg and Pb were determined using ICP-MS. ICP-OES was sometimes required for determining the concentrations of Cu, Zn, Ba and Pb in leachate where the concentrations of these metals were more than or equal to $1mgL^{1-}$.

Wavelengths, isotopes, internal standards for each element and the criteria to use either standard addition (SA) or external calibration (EC)) were the same than those used in Chapter 5. Detailed information on ICP-OES and ICP-MS testing was provided in Chapter 3.

Table 8.6 provides the analytical techniques and the analysis procedure used to determine the concentrations of each element in the different leachates examined. For example, the determination of Si concentrations in all leachates was carried out using ICP-OES. However, the determination of B concentrations was carried out using ICP-OES, ICP-MS External Calibration and ICP-MS Standard Addition depending upon leachate type.

The concentrations reported were calculated by averaging the net concentrations of three identical samples. The black reading was subtracted from the sample concentration reading to provide the net concentration. For each leaching series, three blacks were used and the averaged value of these three blacks was used to calculated net concentrations.

Table 8.6. Analysis details for all elements examined

	⊕ ICP-OES ◇ ICP-MS External Calibration ⊞ ICP-MS Standard Addition							
	pH(28) $C_{85\%}$-$S_{50\%}$	Ion(28)	Rain(28)	pH_{ac}(1)	pH_{ac}(90)	pH(90)	$C_{100\%}$-$S_{100\%}$	$C_{100\%}$-$S_{50\%}$
Si	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
Ca	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
Na	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
K	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
Fe	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
Mg	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
Al	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
B	⊞,◇	⊞	⊞	◇	◇	⊞,◇⊞	⊞,◇⊞	⊞,◇⊞
Cr	⊞	⊞	⊞	◇	◇	⊞	⊞	⊞
Mn	⊞,◇	⊞	⊞	⊕,◇	⊕,◇	⊞,◇	⊞,◇	⊞,◇
Co	⊞	⊞	⊞	◇	◇	⊞	⊞	⊞
Ni	⊞	⊞	⊞	⊕,◇	⊕,◇	⊞	⊞	⊞
Cu	⊕,◇	⊞,◇	⊞	⊕,◇	⊕,◇	⊕,◇	⊞,◇	⊞,◇
Zn	⊕,◇	◇	◇	⊕	⊕	⊕,◇	⊕,◇	⊕,◇
As	⊞	⊞	⊞	⊞	⊞	⊞	⊞	⊞
Se	⊞	⊞	⊞	⊞	⊞	⊞	⊞	⊞
Mo	⊞	⊞	⊞	⊞	⊞	⊞	⊞	⊞
Cd	⊞	⊞	⊞	⊞	⊞	⊞	⊞	⊞
Sn	⊞	⊞	⊞	⊞	⊞	⊞	⊞	⊞
Ba	◇	◇	◇	⊕,◇	⊕,◇	◇	◇	◇
Hg	⊞	⊞	⊞	⊞	⊞	⊞	⊞	⊞
Pb	◇	⊞,◇	◇	⊕	⊕	⊞,◇	⊞,◇	⊞,◇

8.2.3.2.1 Reference Home Material

Reference materials are used to ensure similar measuring conditions for all analyses that are carried out at different times. Because the determination of leachate concentrations from mortar specimens was conducted at different times, there was a need for employing a reference material. Attempts were made to use a commercial certified reference material such as those used for determination of different polluted

water. However, the concentrations of available commercial certified materials differed considerably from the leachate concentrations of mortar specimens containing MSWI-BA. Thus, it was decided to develop a home reference material (HRM) that possessed a matrix composition similar to the leachates from mortar specimens. The concentration of the home reference material was measured at the beginning and at the end of each analysis.

The HRM was prepared by leaching a mixture of cement, MSWI-BA with ∅<212μm, M class sand and MSWI-BA with 212μm<∅<2.36mm and de-ionised water. The liquid to solid ratio was equal to 50. The composition of solid mixture consisted of 21.25%, 3.75%, 32.50% and 32.50% of cement, MSWI-BA with ∅<212μm, class M sand and MSWI-BA with 212μm<∅<2.36mm respectively. The duration of leaching for HRM was 30 minutes and the pH was kept at 4 approximately by adding a few drops of HNO_3. Stirring agitation was used. After 30 minutes, the leachate was separated from the solid by filtration. The leachate was then acidified with HNO_3 to achieve a pH around 2. It was observed that a white precipitated solid could appear in the HRM after six months from preparation. Therefore, a new HRM was prepared every three months.

Table 8.7 and Table 8.8 show the average concentrations, standard deviations and relative standard deviations for the five different HRM solutions used throughout the determination of metals in leachates.

Table 8.7 shows that there was a good repeatability of concentration between the five RHM prepared for elements that were analysed using ICP-OES. Thus, relative standard deviations were only high for those elements whose concentrations were below $5mgL^{1-}$. Contrarily, Table 8.8 shows that the repeatability was not good between the five RHM prepared for the elements that were analysed using ICP-MS Thus, absolute and relative standard deviations were very high for most of element. The relative standard deviations were only below 10% for Mn, Ni, Se and Sn.

Table 8.7. Concentrations and standard deviations of Si, Ca, Na, Fe, Mg, Al, Pb and Zn for the home reference material solutions using ICP-OES

	Concentration in mgL^{1-}		
	Concent.	STDEV[a]	RSDEV(%)[b]
Si	125.28	6.96	5.56
Ca	1576.67	31.06	1.97
Na	17.59	0.75	4.26
K	29.95	0.16	0.52
Fe	1.24	0.24	19.20
Mg	14.60	0.67	4.59
Al	4.55	0.52	11.54
Pb	1.59	0.10	6.17
Zn	2.51	0.50	19.82

[a] Standard Deviation

[b] Relative Standard Deviation

Table 8.8. Concentrations and standard deviations of B, Cr, Mn, Co. Ni, Cu, As, Se, Mo, Cd, Ba, Cd, Sn and Hg for the home reference material solutions using ICP-MS

	Concentration in μgL^{1-}		
	Concent.	STDEV	RSDEV(%)
B(11)	100.9	45.86	45.45
Cr(52)	108.98	23.44	21.51
Mn(55)	470.00	45.15	9.61
Ni(58)	18.49	1.42	7.66
Co(59)	9.56	2.26	23.61
Ni(60)	20.51	2.26	11.01
Cu(65)	319.02	94.45	29.61
As(75)	3.49	1.78	51.08
Se(82)	6.64	0.46	6.87
Mo(95)	15.09	2.16	14.31
Cd(114)	7.49	1.48	19.81
Sn(120)	11.26	0.30	2.70
Ba(138)	603.42	88.94	14.74
Hg(202)	1.95	1.00	51.35

8.2.3.2.2 Determination of Detection Limits

Detection limits were determined for each leaching procedure and were calculated by multiplying three times the standard deviation obtained from the concentrations of the five blanks analysed for each leaching series. The blank concentrations for those elements analysed with ICPP-OES technique were measured using external calibration whereas standard addition method was used for elements analysed with ICP-MS.

Table 8.9and Table 8.10 provide the detection limits for all elements studied, expressed in mgL^{1-} and μmL^{1-} respectively.

Detection limits for all elements examined using ICP-OES were very low. In general, all detection limits were less than $1mgL^{1-}$. Detection limits of Ca, Na and K were only exceptionally higher than $1mgL^{1-}$ for leaching procedures ion(28), $pH_{ac}(28)$ and $pH_{ac}(90)$.

Table 8.9. Detection limits using ICP-OES

	Concentrations in the detention limit in mgL^{1-}								
	pH(28)	Ion(28)	Rain(28)	$pH_{ac}(1)$	$pH_{ac}(90)$	pH(90)	$C_{100\%}$-$S_{100\%}$	$C_{100\%}$-$S_{50\%}$	$C_{85\%}$-$S_{50\%}$
Series	**L2, L3**	**L3**	**L3**	**L1**	**L1, L2**	**L2**	**L4**	**L4**	**L4**
Si	0.147	0.125	0.001	0.0073	0.001	0.158	0.113	0.104	0.147
Ca	0.520	9.051	0.369	1.377	0.001	0.237	1.265	0.250	0.520
Na	0.379	1.023	0.153	0.051	0.001	0.450	0.841	0.546	0.379
K	0.017	0.963	0.034	2.009	1.602	0.036	3.798	0.021	0.017
Fe	0.042	0.012	0.001	0.058	0.024	0.002	0.003	0.000	0.042
Mg	0.000	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000
Al	0.063	0.782	0.001	0.162	0.001	0.078	0.194	0.491	0.063
Ba	N/A	N/A	N/A	0.001	0.001	N/A	N/A	N/A	N/A
Ni	N/A	N/A	N/A	0.007	0.001	N/A	N/A	N/A	N/A
Pb	N/A	N/A	N/A	0.001	0.001	N/A	N/A	N/A	N/A
B	N/A	N/A	N/A	0.02	0.003	N/A	N/A	N/A	N/A
Mn	N/A	N/A	N/A	0.003	0.004	N/A	N/A	N/A	N/A
Cu	0.013	N/A	N/A	0.008	0.078	0.018	N/A	N/A	0.013
Zn	0.051	N/A	N/A	0.013	0.032	0.001	0.020	0.009	0.051

Detection limits for elements analysed using ICP-MS (Table 8.10) varied widely for each element and leaching procedures used. For example the concentrations in the limits of detection for B, Ni and Pb varied significantly for each leaching procedure. The detection limits of Cu and Zn were exceptionally high for all leaching procedures. For example, for the leaching procedure that used de-ionised water as leachant (Ion(28)), the concentration in the detection limit for Zn was equal to $82\mu gL^{1-}$. Controversially, the concentrations in the limit of detection for Cr, Co, As and Se were lower than $1\mu gL^{1-}$ for all leaching procedures. In addition, limits of detection were relatively low for Cd, Sn and Hg. The limit of detections of Mn, Mo and Ba were low for most all the analysis.

Table 8.10. Detection limits using ICP-MS

	Concentrations in the detection limit in μgL^{1-}								
	pH(28)	Ion(28)	Rain(28)	$pH_{ac}(1)$	$pH_{ac}(90)$	pH(90)	$C_{100\%}$-$S_{100\%}$	$C_{100\%}$-$S_{50\%}$	$C_{85\%}$-$S_{50\%}$
Series	L2, L3	L3	L3	L1	L1, L2	L2	L4	L4	L4
B^{10}	8.004	3.930	8.998	8.030	0.852	10.116	3.353	12.080	8.004
Cr^{52}	0.027	0.765	0.811	0.650	0.125	0.012	0.533	0.020	0.027
Mn^{55}	0.813	3.822	21.288	2.268	0.390	0.110	0.748	0.780	0.813
Co^{59}	0.246	0.038	0.195	0.075	0.039	0.739	0.011	0.002	0.246
Ni^{60}	6.963	1.044	0.334	2.032	3.365	8.721	1.084	0.738	6.963
Cu^{65}	30.273	22.950	12.253	33.604	79.068	28.623	24.112	15.660	30.273
Zn^{66}	27.761	82.104	63.694	19.250	17.303	31.282	51.877	57.508	27.761
As^{75}	0.859	0.121	0.645	0.016	0.016	0.260	0.523	0.450	0.859
Se^{82}	0.515	0.340	1.024	0.393	0.111	0.121	0.235	0.210	0.515
Mo^{95}	0.717	17.760	1.792	0.070	0.001	0.021	0.080	0.027	0.717
Cd^{114}	0.648	0.186	3.128	0.058	0.292	0.148	2.061	0.121	0.648
Sn^{120}	0.529	1.452	1.490	0.535	0.958	0.163	2.075	0.900	0.529
Ba^{138}	1.093	1.903	51.433	0.958	0.215	0.641	1.751	0.836	1.093
Hg^{202}	0.298	1.456	0.918	0.444	0.182	0.058	0.242	0.319	0.298
Pb^{208}	1.165	6.319	4.534	5.893	1.647	0.127	7.496	2.940	1.165

8.2.3.2.3 Controlling Parameters during Analysis

The use of controlling parameters during analysis was required to identity the possible instrumental shifting. As discussed in Chapter 5, blanks and standards solutions were tested a few times while sample testing was being carried out. Thus, if their concentrations varied by more than 5% compared with the previous reading, a cleaning procedure followed by a new calibration was conducted.

8.2.3.2.4 Analysis Sequence

Determination of concentrations of 22 elements requires an appropriate sequential manner to ensure that the analysis is carried out accurately. Shifting of signal, residual contamination and contamination caused from one sample to the others are factors that need to be identified.

Figure 8.2 shows a flow diagram of the methodology that was used for analysing metal elements using ICP-OES and ICP-MS techniques. Turning solutions were run to check if specific instrumental parameter values were in the recommended range given in the

specifications of the instruments. If turning solutions gave appropriate operational conditions, instruments were calibrated according to the sample concentration ranges. After the calibration of instruments, a few standard solutions and blanks were run as controlling parameters. Next, home reference material (HRM) solutions were run to check their repeatability with the previous analysis. If HRM reading were similar to those for previous days, 5 new samples were analysed. After that, measuring conditions were tested again by running the controlling parameters. If controlling parameter readings were similar to the previous readings, another 5 test samples were run. But, if the controlling parameter readings differed by more than 5%, the instrument were cleaned with a solution of 5% HNO_3. Figure 8.2 shows the sequence followed during the analysis of all elements examined.

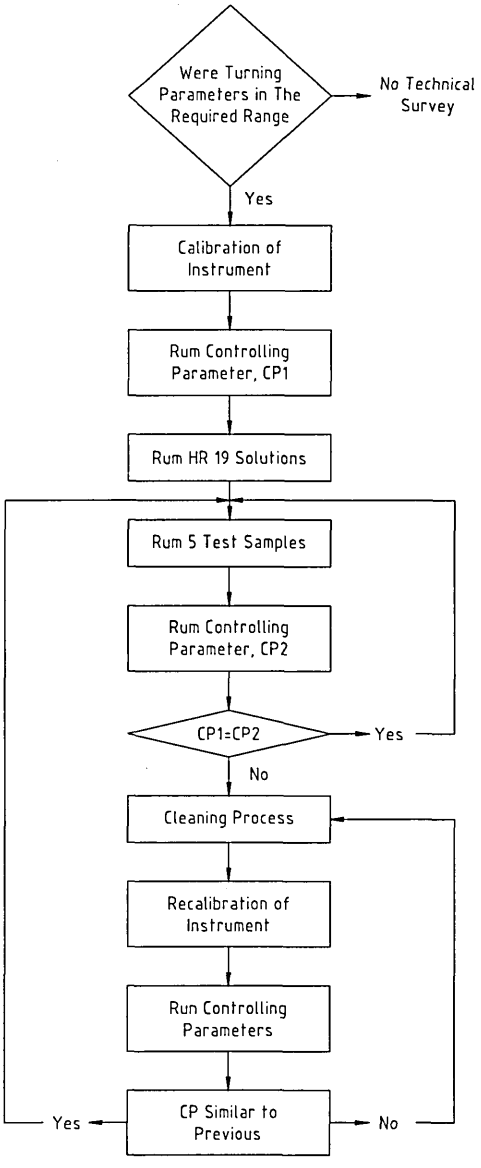


Figure 8.2. Flow diagram of the analysis methodology

8.2.3.3 Determination of Sulfates and Chlorides

Sulfates and chlorides concentrations were determined using ion chromatography technique. Details of ion chromatography procedure were given in Chapter 3. Concentrations of SO_4^{2-} and Cl^- could not be determined in leachates obtained by carrying out the acidic leaching procedure (e.g. $pH_{ac}(28)$, $pH_{ac}(90)$, and $pH_{ac}(1)$), which were used for series L1 and L2. The addition of HNO_3 acid during test impeded to identify the peaks of SO_4^{2-} and Cl^{1-} in the chromatograph.

Net concentrations of sulfates and chlorides reported were calculated by averaging the concentrations obtained from the three identical leachates used for each test. A good reproducibility between the three identical leachates was obtained.

8.3 RESULTS AND DISCUSSION OF RESULTS

8.3.1 Concentrations of Ca, Si, Al, Mg, Fe, Na and K

8.3.1.1 Series L1

Figure 8.3 shows the cumulative (CC) and relative (CC) concentrations of Ca, Si, Al, Mg, Fe, K and Na in the leachates for mortar specimens cured initially for 1 and 90 days. Mortar contained 15% and 50% of MSWI-BA as partial replacements the cement and respectively. The RC are referred to the concentrations obtained at 6h, 24h, 3, 7 and 14 days since the test started.

- Cumulative concentrations (CC)

Concentrations of Ca were similar in the leachates examined regardless of initial curing of the mortar specimens. Concentrations of Si, Al, Mg and Fe were slightly higher in leachates from mortar specimens cured for 90 days ($pH_{ac}(90)$) than those from specimens cured for 1 day ($pH_{ac}(1)$). Controversially, concentrations of K and Na were higher in leachates from specimens cured for 1 days than those from specimens cured for 90 days. The higher concentrations of Si, Al, Mg, Fe in the leachates for $pH_{ac}(90)$ specimens compared with $pH_{ac}(1)$ specimens were not expected. These un-expected results can be linked with those observed in Chapter 7, where mortar specimens cured initially for short period (i.e. 2 days) exhibited lower sulfate deterioration than specimens cured for long initial periods (i.e. 90 days). This correspondence between sulfate resistance and leaching behaviour has been discussed in details in section 8.3.4.

- Relative concentrations

In general, leachate relative concentrations of all elements in leachates from $pH_{ac}(1)$ and $pH_{ac}(90)$ specimens exhibited similar trend during the 14 days of the leaching test.

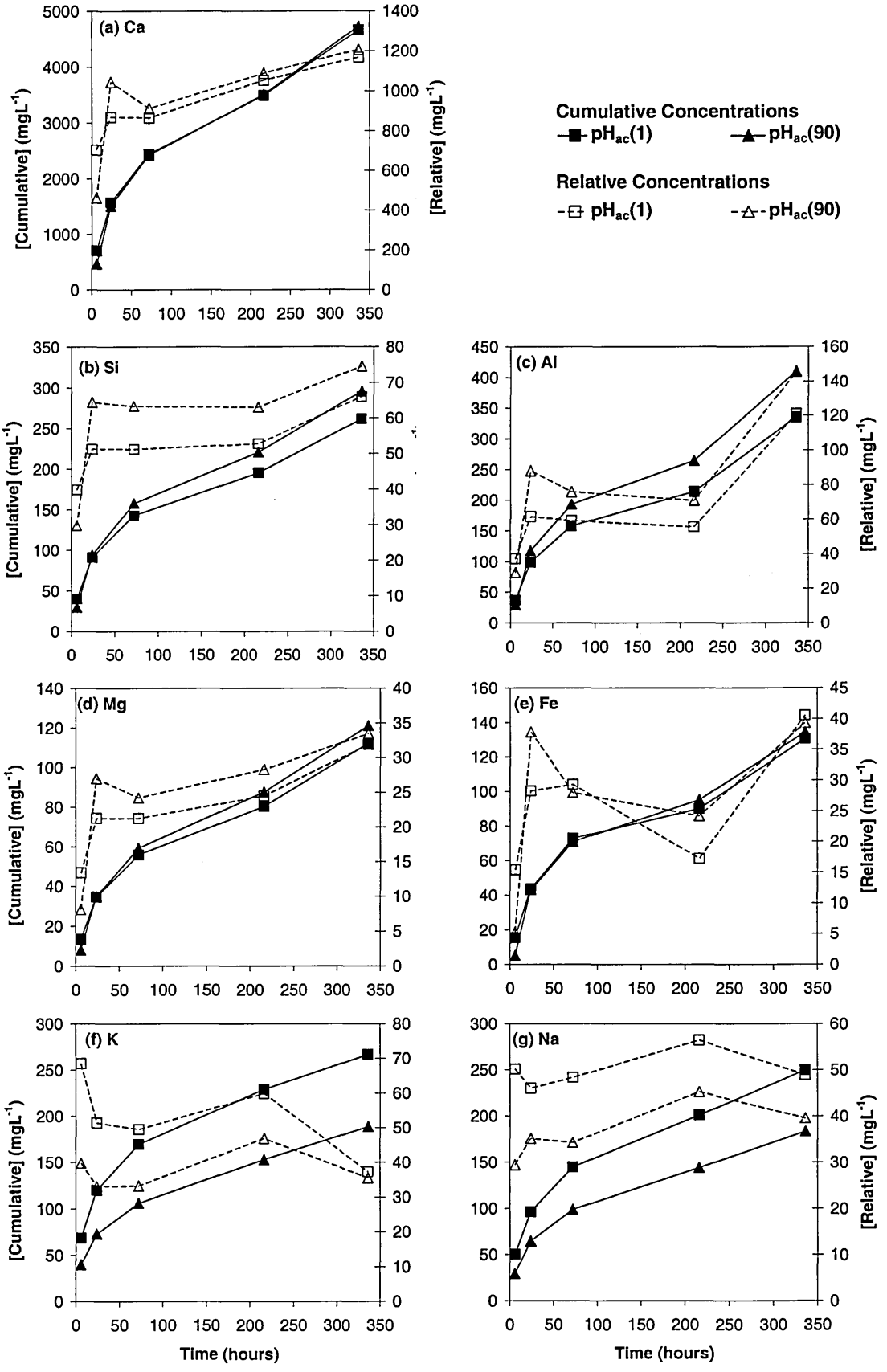


Figure 8.3. Cumulative and relative concentrations of Ca, Si, Al, Mg, Fe, K and Na, in leachates for mortar containing MSWI-BA cured initially for 1 and 90 days (series L1)

8.3.1.2 Series L2

Figure 8.4 shows the cumulative concentrations, in logarithmic scale, of Ca, Si, Al, Mg, Fe, K and Na in leachates of mortar specimens using leaching procedures that were carried out with and without adding acid during the test (14 days). Mortar specimens cured for 90 days were used for this series. For this series (L2), the RC were not discussed as they are explained in other leaching series (e.g. L1 and L3). Mortar contained 15% and 50% of MSWI-BA as partial replacements the cement and respectively. The Fe CC pH(90) are not given in Figure 8.4(e) because their values were less than $1 mgL^{1-}$.

The addition of acid during leaching increased the concentrations considerably of Ca, Si, Al, Mg, and Fe in the leachates. Thus, the leachate concentrations for $pH_{ac}(90)$ were approximately 10 times higher than those for pH(90). In contrast, the CC of K and Na were not affected by the addition of acid. These results suggested that K and Na leaching behaviours were less dependent on the leachant pH than Ca, Si, Al, Mg, and Fe. Thus, results of leaching series L2 suggested that small additions of acid during test can cause significant difference in the leachate concentrations of Ca, Si, Al, Mg and Fe.

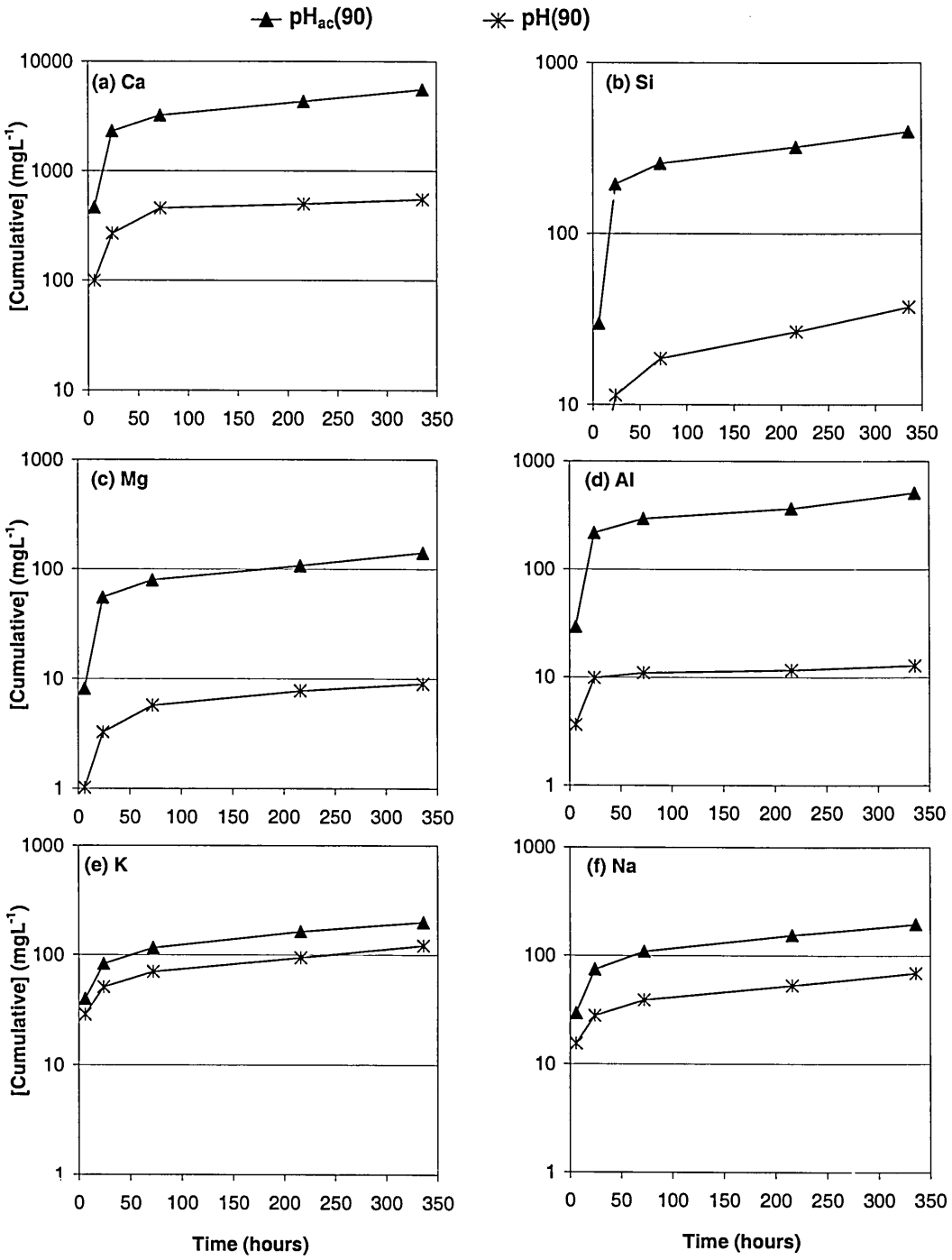


Figure 8.4 Cumulative concentrations Ca, Si, Al, Mg, Fe, K and Na in leachates for mortar containing MSWI-BA leached out with and without addition of acid during the test (series L2)

8.3.1.3 Series L3

Figure 8.5 shows the CC and RC of Ca, Si, Al, Mg, K and Na in leachates of mortar specimens using three different leachants. The leachants were rain water (rain(28)), de-ionised water (ion(28)) and an acidic solution of de-ionised water with a pH of approximately 2 (pH(28)). Mortar specimens contained 15% and 50% of MSWI-BA as partial replacements the cement and respectively and were initially cured for 28 days.

For rain(28) and ion(28) leachates, the Fe and Mg CC and RC were not significant, therefore they are on the "x" axes.

- Cumulative concentrations (CC)

Generally, there was not much difference in the cumulative concentrations when either rain or de-ionised water was used as leachants. For all the elements examined, leachate concentrations using rain(28) and ion(28) procedures were lower than those using pH(28). The difference in concentrations between pH(28) and rain(28) or ion(28) leachates was significant high for Ca, Si, Fe and Mg. The CC of Al were similar for the three leachants at the end of each leaching procedure. The CC of K and Na were approximately 20mgL^{1-} higher for procedure pH(28) than for that of rain and de-ionised water.

- Relative concentrations (RC)

Rain and de-ionised leachates exhibited similar trend in relative concentrations for all the elements examined. The RC of Ca, Si and Al exhibited a slight increase in concentration during the test. The RC of Na and K decreased up to 72 hours before they started to increase until the end of the test.

For the procedure pH(28) the trend was different than that observed for rain(28) and ion(28). The RC of Ca increased up to 24 hours and then they decreased drastically up to approximately 200 hours. Afterwards they remain constant up to the end of the leaching procedure. Si RC increased significantly during the first 24 hours. A slight decrease was observed after that until 72h. After that there was a slight increase in RC until the end of the test. The RC of Al exhibited a large increase in RC up to 24 hours and a decrease from 24 hours to 72 hours. After 72 hours the RC decreased slightly. The RC of Mg increased significantly up to 24 hours and after that they decreased or increased slightly until the end of the test. Fe RC increased significantly up to 24 hours. From 24 to 72 hours they showed a noticeable decrease and afterwards they increased slightly until the end of the test. The RC of Na and K showed similar trend than for rain water or deionised water procedures.

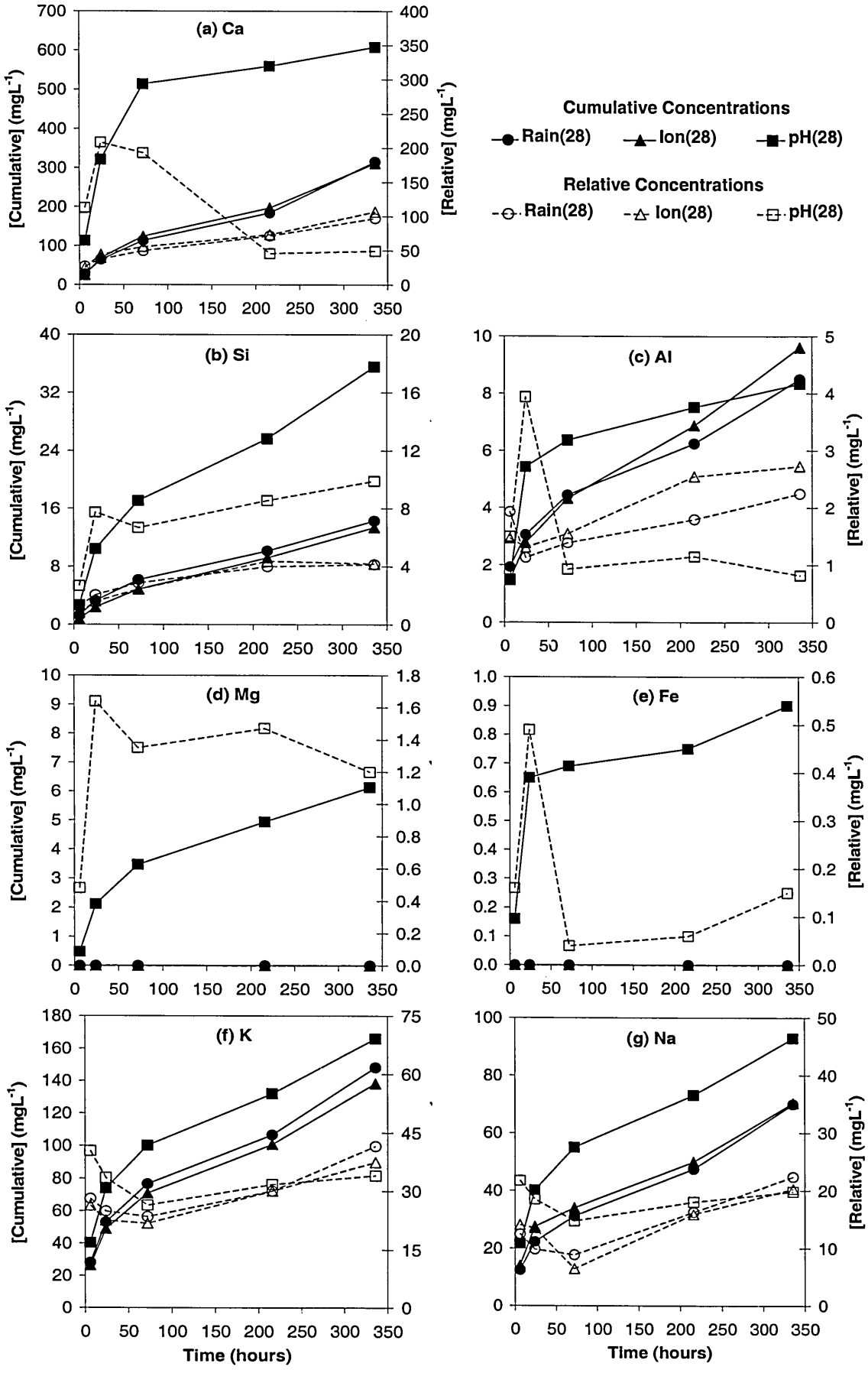


Figure 8.5 Cumulative and relative concentrations of Ca, Si, Al, Mg, K and Na in leachates for mortar containing MSWI-BA using three leachants (series L3)

8.3.1.4 Series L4

Figure 8.6 show the cumulative and relative concentrations of Ca, Si, Al, Mg, Fe, K and Na in leachates from three mixes containing different MSWI-BA replacement levels. The three different mixes were; a mix contained 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively ($C_{85\%}$-$S_{50\%}$); second mix contained 50% of MSWI-BA as relative replacement of sand ($C_{100\%}$-$S_{50\%}$) and the third mix consisted of the reference mix that contained with 100% of cement and sand ($C_{100\%}$-$S_{100\%}$). All mixes were cured for 28 days before the test started.

- Cumulative concentrations (CC)

Cumulative concentrations of Ca were slightly higher in leachates from the reference mix ($C_{100\%}$-$S_{100\%}$) specimens followed by $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{50\%}$. The decrease in Ca concentration may be associated with the decrease in $Ca(OH)_2$ production caused by the pozzolanic reactivity of MSWI-BA used as replacement of cement and sand. However, this effect was not clear. Leachates from $C_{100\%}$-$S_{100\%}$ and $C_{100\%}$-$S_{50\%}$ gave similar CC of Si, which were slightly higher than that for $C_{85\%}$-$S_{50\%}$. Al, Mg, Fe, K and Na CC were the highest in leachates from $C_{85\%}$-$S_{50\%}$ followed by $C_{100\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{100\%}$ leachates. These results indicated that the partial replacement of cement and sand with MSWI-BA caused an increase in leachate concentrations for Al, Mg, Fe K and Na.

- Relative concentration (RC)

Generally, the trends in relative concentration were similar in the leachates from the three different mixes. The RC of Ca increased up to 72 hours from the test started. After that they decreased sharply and then remained constant until the end of the test. Si RC increased during the first 72 hours. After that they exhibited slight increase until the end of the test. The RC of Al showed different trend for leachates from specimens containing MSWI-BA to that of the reference specimens. $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-S_{50} leachates exhibited a notable increase in RC for the first 24 hours and a notable decrease from 24 hours to 72 hours. After 72 hours, the RC remained constant. Leachates from $C_{100\%}$-$S_{100\%}$ mix exhibited a slight increase during the first 24 hours and slight decrease from 200 hours until the end of the test. Mg RC increased up to 24 hours and after that they decreased until the end. K and Na RC exhibited the same trend. Concentrations decreased slightly for the first 72 hours and increased slightly until the end of the test.

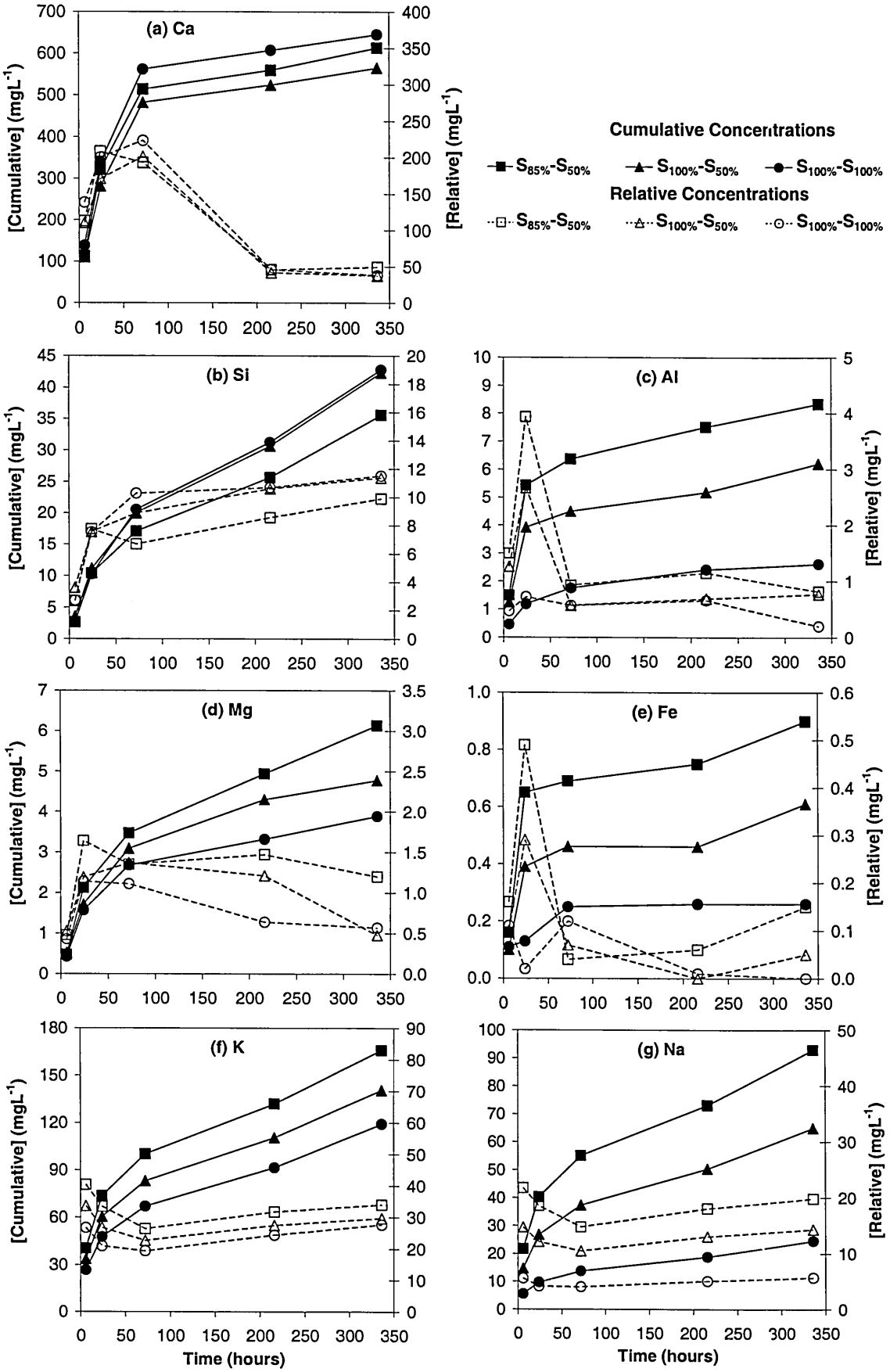


Figure 8.6. Cumulative and relative concentrations of Ca, Si , Al, Fe, Mg, K and Na in leachates for mortar containing various MSWI-BA replacements (series L4)

8.3.2 Concentrations of B, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Ba, Hg and Pb

8.3.2.1 Series L1

Figure 8.7 shows cumulative and relative concentrations of B, Co and Cr in leachates that were obtained by adding acid during leaching test. Mortar specimens contained 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively and were initially cured for 1day and 90 days before starting the leaching test.

- Cumulative concentrations (CC)

Concentrations of B in leachates from specimens cured for 1 day were only slightly higher than those from $pH_{ac}(90)$ specimens. Cr concentrations were not affected by the length of the initial curing. Concentrations of Co were higher for leachates from $pH_{ac}(90)$ specimens than those for $pH_{ac}(1)$ leachates. The difference in Co concentrations for the different curing used was approximately 25μgL^{1-} at the end of the leaching procedure.

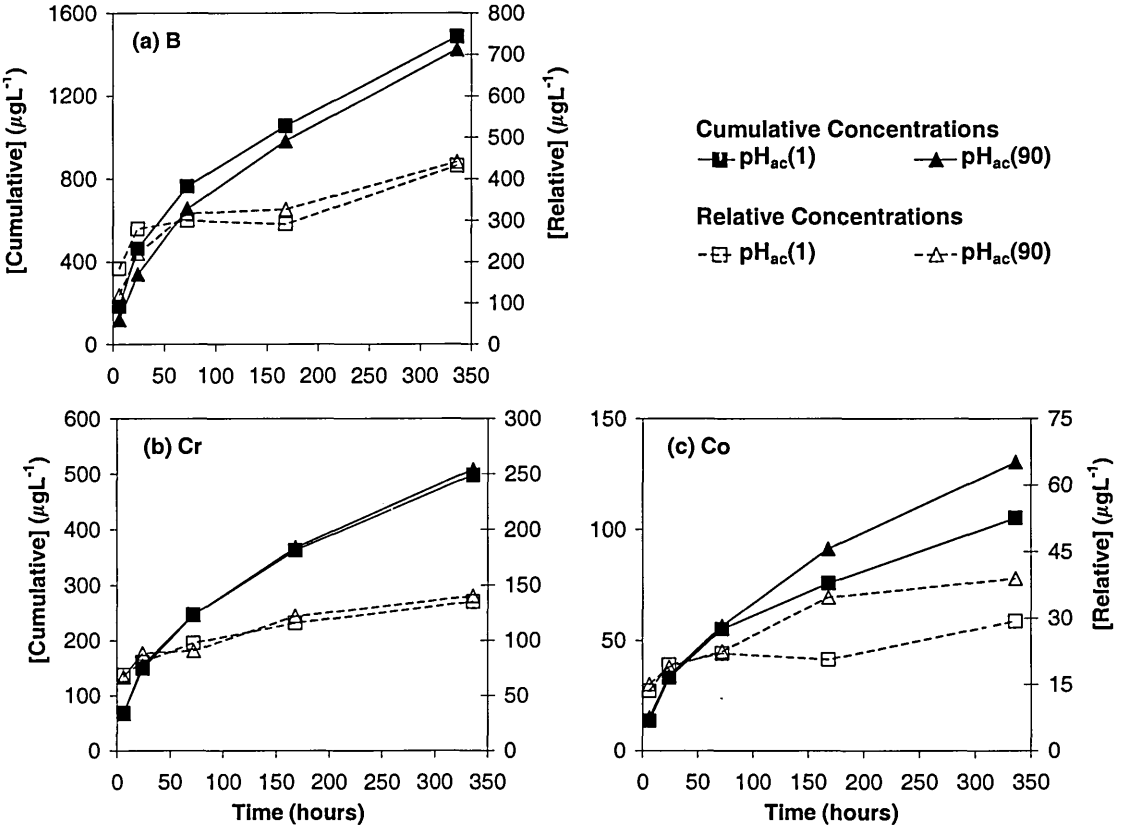


Figure 8.7. Cumulative and relative concentrations of B, Cr, and Co in leachates for mortar containing MSWI-BA cured initially for 1 and 90 days (series L1)

- Relative concentrations (RC)

The trend in RC for B and Cr were similar for the both initial curing period examined, whereas for Co, the trends were slightly different. B and Cr RC showed a sharp increase during the first either 24 or 72 hours and after that the increase was shallower.

Figure 8.8 shows cumulative and relative concentrations of Cd, Se, Mo, Sn and As in leachates for leaching series L1.

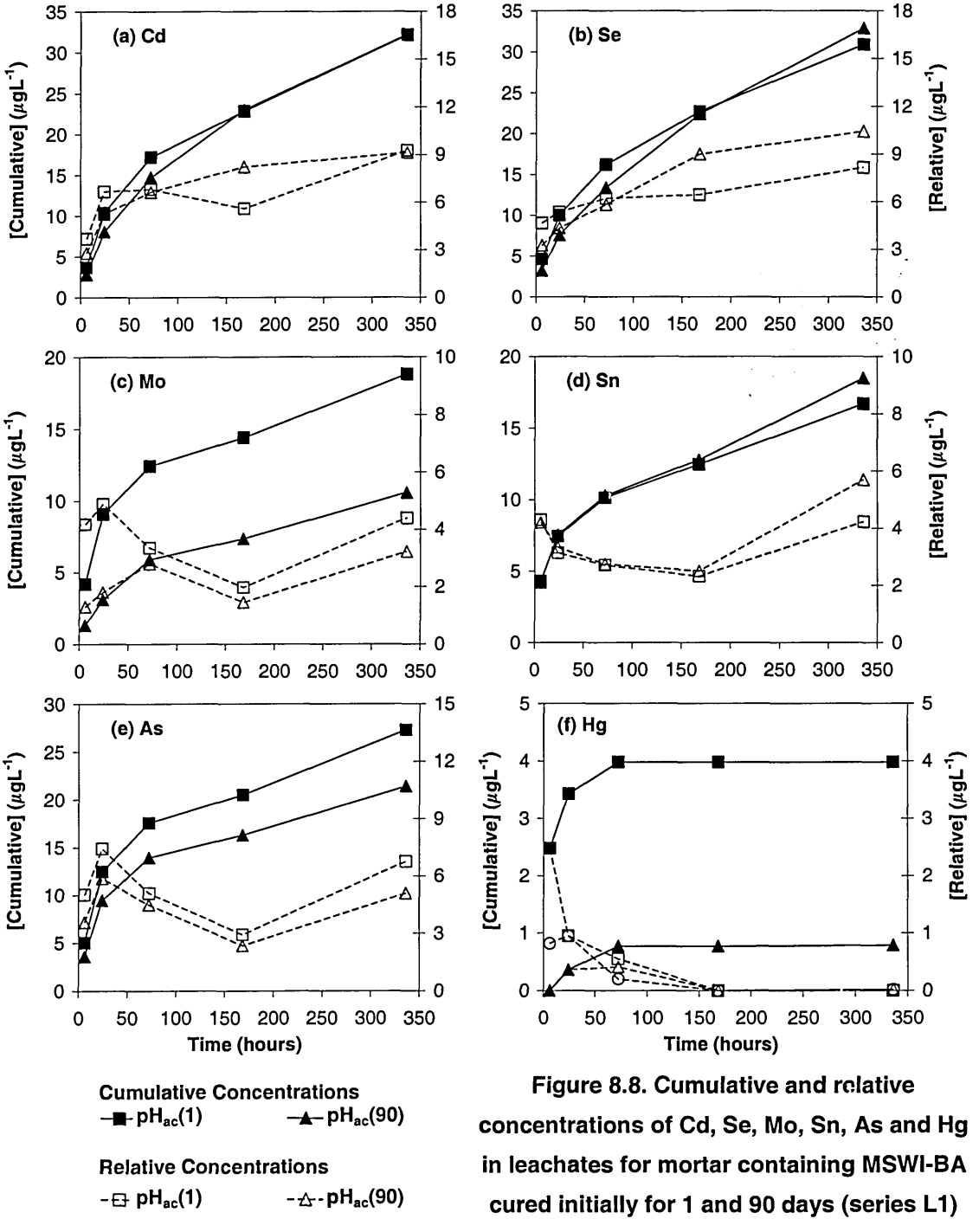


Figure 8.8. Cumulative and relative concentrations of Cd, Se, Mo, Sn, As and Hg in leachates for mortar containing MSWI-BA cured initially for 1 and 90 days (series L1)

- Cumulative concentrations

Concentrations of Cd, Se and Sn were similar in the leachates regardless initial curing of specimens (i.e. 1 and 90 days). This indicated that the curing period of mortar specimens before leaching did not influence the leachability of these elements. These CC were approximately 33μgL^{1-} for Se and Cd and 17μgL^{1-} for Sn at the end of the test. On the other hand, concentrations of Mo, As and Hg were dependent on the initial curing period. Leachates from $pH_{ac}(1)$ specimens exhibited higher concentrations than those leachates from $pH_{ac}(90)$ specimens. These results indicated that the increase in initial curing period caused a decrease in leachability of these elements.

- Relative concentrations (RC)

RC of Cd and Se were dependent on duration of specimens initial curing. However, Mo, Sn and As RC exhibited similar trend for the two different initial curing. RC of Hg showed that most of Hg was leached out during the first 72 hours.

Figure 8.9 shows cumulative, CC and relative concentration, RC, in mgL^{1-}, of Mn, Ba, Ni, Cu, Zn and Pb in leachates for leaching series L1.

- Cumulative concentrations (CC)

There was not any difference in CC of Mn and Ba in leachates from specimens cured for different periods. Concentrations of Mn and Ba were approximately 7 and 5mgL^{1-} respectively at the end of the test. Contrarily, Ni, Cu, Zn and Pb concentrations were slight different. Ni concentrations were higher in leachates from $pH_{ac}(1)$ specimens that those from $pH_{ac}(90)$ specimens, whereas concentrations of Cu, Zn and Pb were higher in leachates from $pH_{ac}(90)$ specimens.

- Relative concentrations (RC)

In general, similar trend in RC of all the elements examined was observed for leachates from the specimens cured for either 1 or 90 days. RC of Zn and Pb at 200 hours of leaching showed different trend between both initial curing periods.

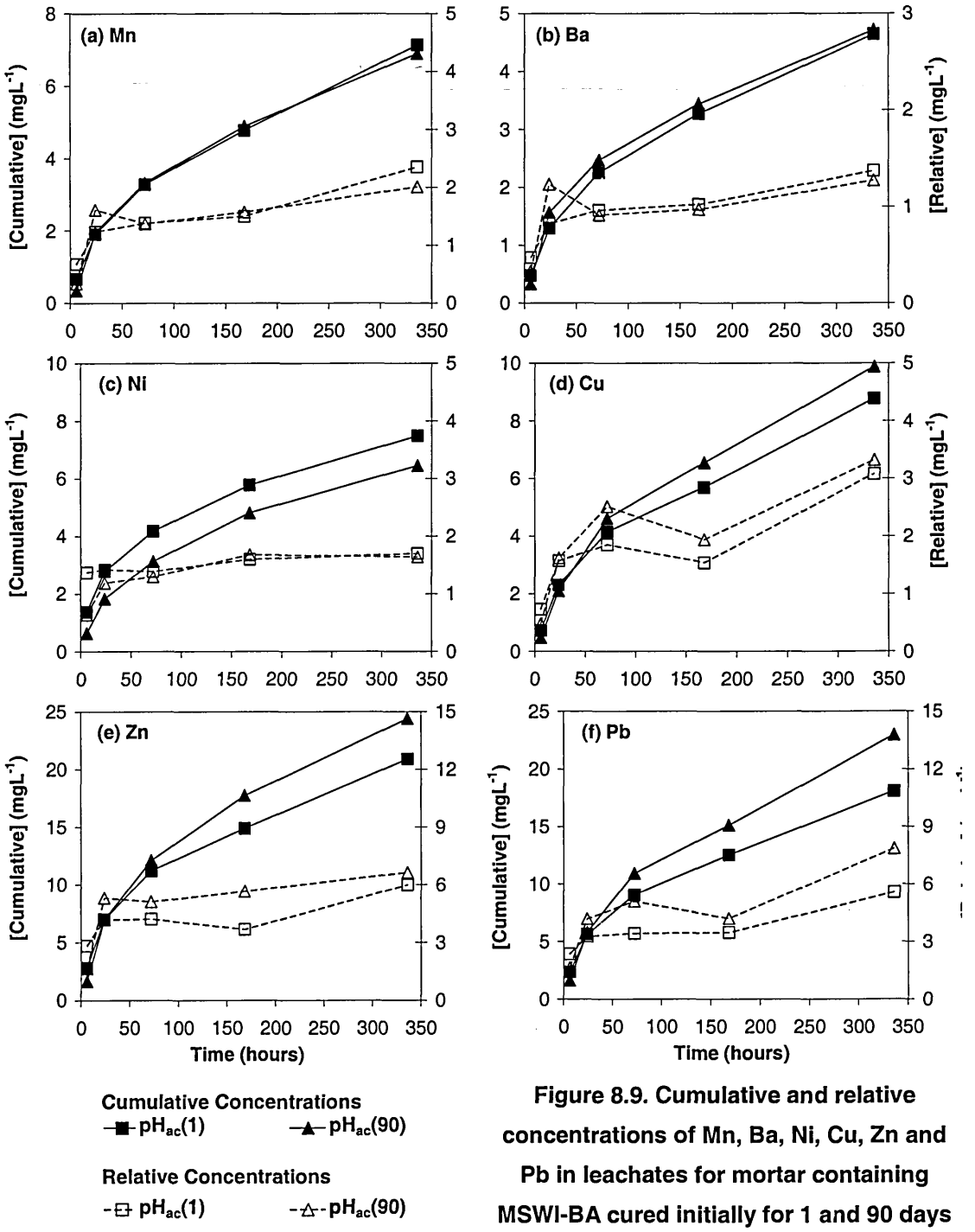


Figure 8.9. Cumulative and relative concentrations of Mn, Ba, Ni, Cu, Zn and Pb in leachates for mortar containing MSWI-BA cured initially for 1 and 90 days (series L1)

8.3.2.2 Series L2

The concentration of B, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Ba, Hg and Pb in leachates from mortar specimens initially cured for 90 days that were leached out without addition of acid during the test, were not able tc analysed.

8.3.2.3 Series L3

Table 8.11 provides cumulative concentrations of B, Mn, Co, Ni, Cu, As, Se, Mo, Cd, Sn, and Hg, expressed in μgL^{1-} at the end of the leaching tests. These concentrations were in leachates of mortar specimens containing 15% and 50% of MSWI-BA as replacement of cement and sand and initially for cured 28 days. The specimens were leached out using three different leachants: rain water (rain(28)); de-ionised water (ion(28)); and acidic deionised water with pH around 2 before contact with the specimen (pH(28)). The table also shows the concentrations in the limit of detection (CDL) for above elements for comparison purposes. Relative concentrations are not shown due to some of them were below limit of detection (BDL) or below $1\mu gL^{1-}$.

Table 8.11. Cumulative concentrations of B, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Ba, Hg and Pb in leachates of mortar for the leaching series L3

	pH(28)		Ion(28)		Rain(28)	
	CDL[a]	CC[b]	CDL	CC	CDL	CC
B	8.00	170.29	3.93	BDL[c]	9.00	BDL
Mn	0.82	133.48	3.82	BDL	21.29	BDL
Co	0.25	6.89	0.04	<1	0.20	<1
Ni	6.96	21.48	1.04	BDL	0.33	5
Cu	30.27	1040.41	22.95	BDL	12.25	BDL
As	0.86	<1	0.12	<1	0.65	<1
Se	0.52	<1	0.34	<1	1.02	<1
Mo	0.72	<1	17.76	<1	1.79	<1
Cd	0.65	<1	0.19	<1	3.13	<1
Sn	0.53	<1	1.45	<1	1.49	<1
Hg	0.30	<1	1.46	<1	0.92	<1

a Concentration in the limit of detection
b Cumulative Concentration in leachates
c Concentration below the concentration in the limit of detection

Concentrations of B, Mn, Co, Ni and Cu were higher in leachates from pH(28) specimens than that from rain(28) and ion(28) specimens. These concentrations were approximately 170, 28, 134, 7, 22, $1040\mu gL^{-1}$ respectively in pH(28d) leachates whereas they were either below the concentration in the limit of detection or below $1\mu gL^{-1}$ for rain(28) and ion(28) leachates. Concentrations of As, Se, Mo, Cd, Sn, and Hg were below $1\mu gL^{-1}$ in the three different leachates (rain(28), ion(28) and pH(28)).

Figure 8.10 shows the cumulative and relative concentrations of Cr, Zn, Ba and Pb in leachates obtained using rain water, de-ionised water and acidic de-ionised water with pH=2 as leachants. Concentrations are expressed in μgL^{1-}.

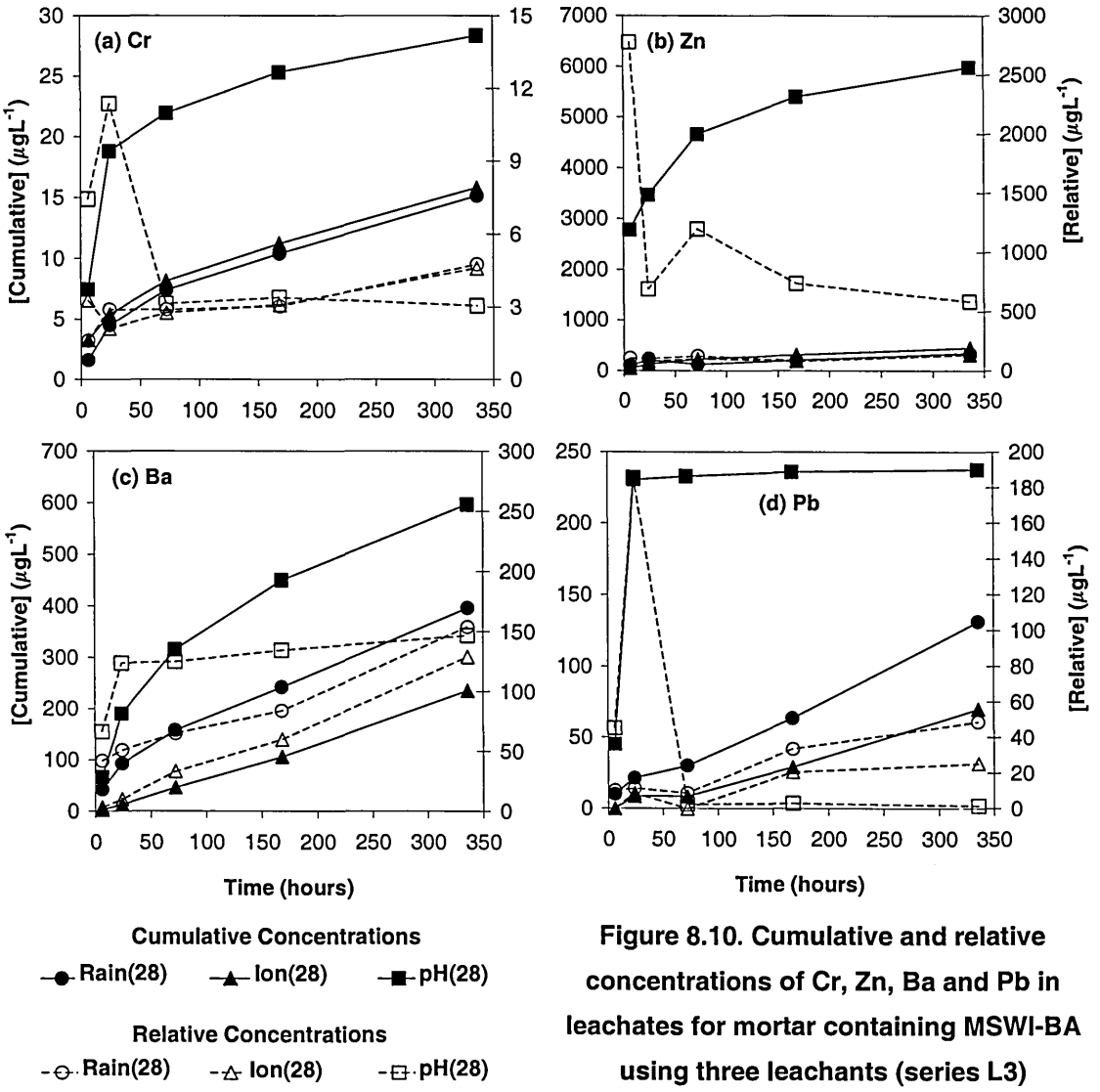


Figure 8.10. Cumulative and relative concentrations of Cr, Zn, Ba and Pb in leachates for mortar containing MSWI-BA using three leachants (series L3)

- Cumulative concentrations (CC)

Generally, CC of the four elements were significantly higher in pH(28) leachates than in ion(28) and rain(28) leachates. The differences in Cr and Zn CC were approximately $10\mu gL^{1-}$ and $5000\mu gL^{1-}$ between pH(28) leachate and ion(28) and rain(28) leachates. Concentrations of Cr and Zn were similar in ion(28) and rain(28)) leachates, whereas Ba and Pb concentrations were slightly different in the same leachates. Ba and Pb concentrations were approximately 200 and $50\mu gL^{1-}$ higher in rain(28) leachates compared with ion(28) leachates. Whilst Ba and Pb concentrations were approximately 200 and $100\mu gL^{1-}$ lower in rain(28) leachates than in pH(28) leachate.

- Relative concentrations (RC)

Trends of RC of Cr, Zn, Ba and Pb were similar for rain(28) and ion(28) leachates. However, these trends were different than those for pH(28) leachates. For rain(28) and ion(28) leachates, RC of Cr and Zn were similar whereas RC of Ba and Pb showed a slight increase throughout the duration of the test. For RC pH(28) leachates, the RC of Cr and Pb exhibited a notable increase during the first 24 hours. From 24 hours to three days they decreased drastically. After that they remained constant until the end of the test. RC of Zn showed that considerable increase in concentration at 6 hours and they kept almost constant for the rest of the leaching period.

8.3.2.4 Series L4

Figure 8.11 show the cumulative and relative concentrations of Mn, Ni, Cu, Ba and Pb in leachates from three mixes with different MSWI-BA replacement. The three different mixes were; a mix contained 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively ($C_{85\%}$-$S_{50\%}$); second mix contained 50% of MSWI-BA as a partial replacement of sand ($C_{100\%}$-$S_{50\%}$) and the third mix consisted of the reference mix that contained with 100% of cement and sand ($C_{100\%}$-$S_{100\%}$). All mixes were cured for 28 days before the leaching test started.

- Cumulative concentrations (CC)

Generally, CC of Mn, Ba and Pb were the highest in leachates for $C_{85\%}$-$S_{50\%}$ specimens, followed by leachates from $C_{100\%}$-$S_{50\%}$ specimens. The Leachates obtained from the reference mix, $C_{100\%}$-$S_{100\%}$, exhibited the lowest concentrations of Mn, Ba, and Pb. These results indicated that the replacement of cement and sand with MSWI-BA caused an increase in leachability of Mn, Ba, and Pb. Ni CC were similar in $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{50\%}$ leachates. This indicated that the major part of leached Ni was from the aggregates as a result of replacing sand with MSWI-BA. The CC of Cu in $C_{100\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{100\%}$ leachates were similar and lower than in $C_{85\%}$-$S_{50\%}$ leachates. This indicated that most of the Cu leached was from replacing the cement with MSWI-BA.

- Relative concentrations (RC)

Leachates from $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{50\%}$ showed similar trend in RC of Mn, Ni, Ba and Pb. RC of Mn, Ni, and Pb exhibited an increase from 6h to 24h and an important decrease from 24h to 72h. After 72h, they remained almost constant until the end of the test. RC of Ba exhibited a significant increase between 6h and 24h and then they remained constant. In $C_{100\%}$-$S_{100\%}$ leachates, RC of Mn, Ba and Pb did not exhibit a significant change during the duration of the test. The trend in RC of Ni was similar to shown in $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{50\%}$ leachates.

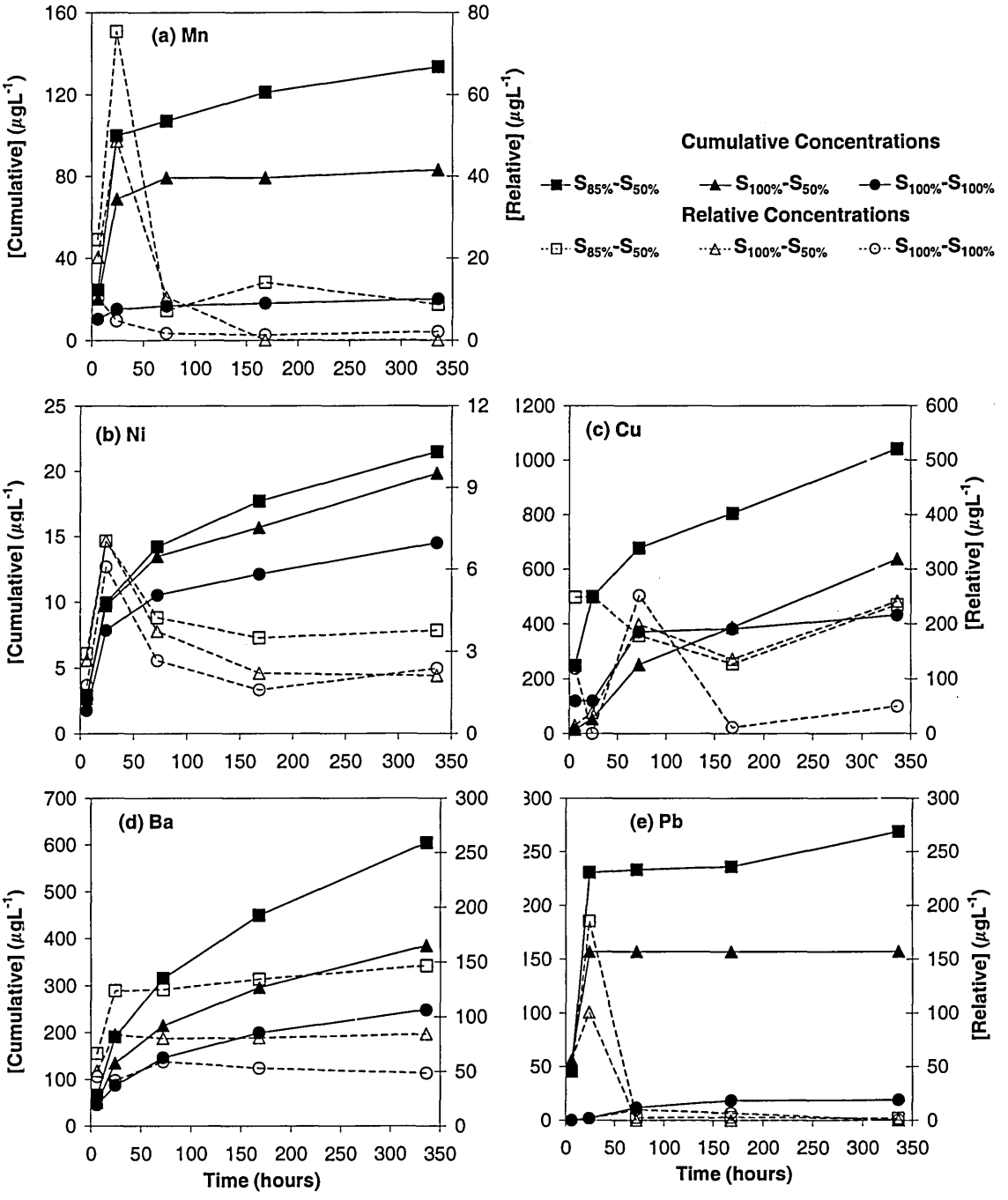


Figure 8.11. Cumulative and relative concentrations of Mn, Ni, Cu, Ba and Pb in leachates for mortar containing various MSWI-BA replacements (series L4)

Figure 8.12 shows cumulative and relative concentrations of B, Cr and Zn in leachates for experimental series L4.

Cumulative and relative concentrations of these elements did not exhibit a common behaviour. It was not shown clearly which of the three mixes either facilitated or impeded the leachability of these elements. For example, CC of B and Zn were quite similar in $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{100\%}$ leachates whilst they were different to the CC in $C_{100\%}$-$S_{50\%}$ leachates. This difference in CC between leachates was not explained. Controversially, mixes containing MSWI-BA as replacement cement and replacement

of cement and sand seemed to impede the dissolution of Cr. Leachates for $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{50\%}$ specimens exhibited slightly smaller CC of Cr than those for $C_{100\%}$-$S_{100\%}$ specimens.

In general RC of the three elements indicated that these elements were mainly leached out during the first 24 hours since test started. After 24 hours the RC did not show a significant change.

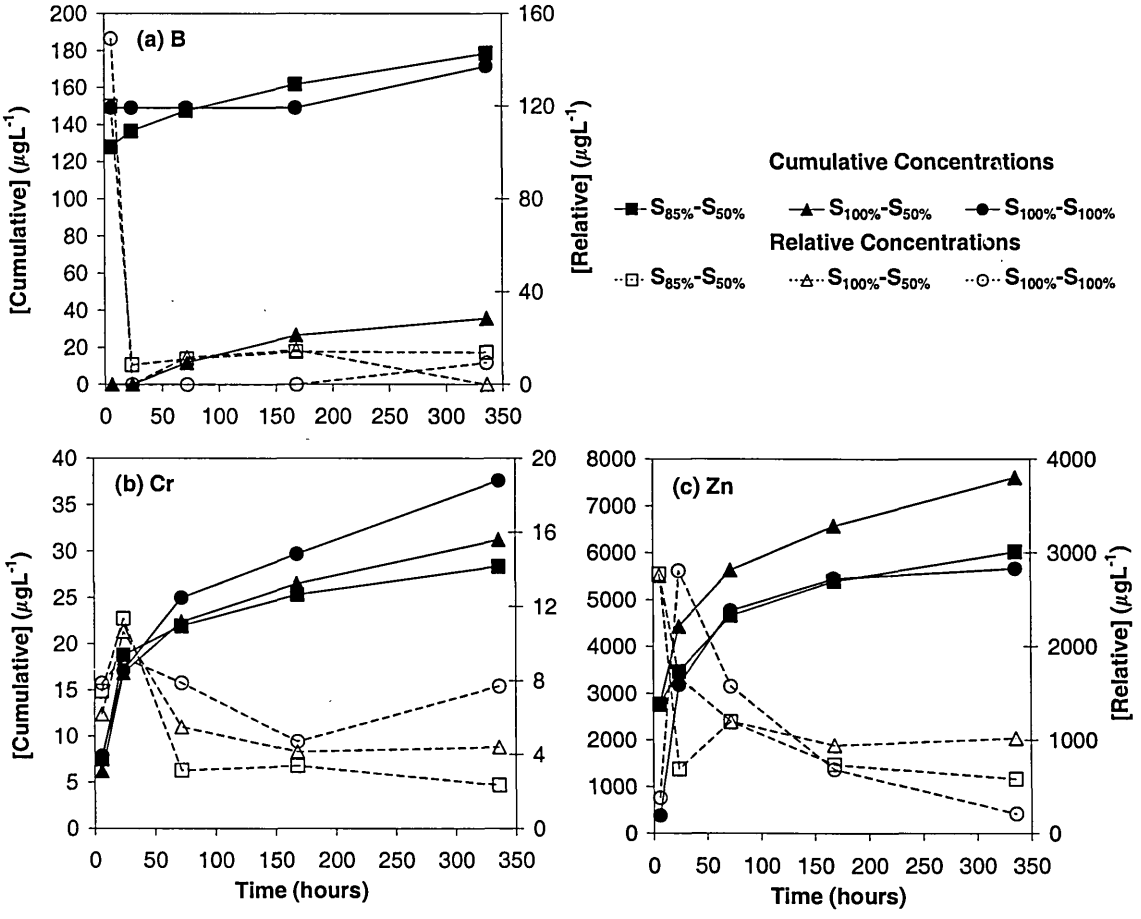


Figure 8.12. Cumulative and relative concentrations of B, Cr and Zn in leachates for mortar containing various MSWI-BA replacements (series L4)

Table 8.12 provides the concentrations of Co, As, Se, Mo, Cd, Sn, and Hg, expressed in μgL^{-1}, for leachates obtained in series L4. All the concentrations examined here, except Co concentration for $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{50\%}$ leachates, were below $1\mu gL^{-1}$. These higher concentrations of Co in $C_{85\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{50\%}$ leachates compared with those in $C_{100\%}$-$S_{100\%}$ were attributed to the partial replacement of cement and sand with MSWI-BA.

Table 8.12. Concentrations of Co, As, Se, Mo, Cd, Sn, and Hg for the leaching series L4

	$C_{85\%}$-$S_{50\%}$		$C_{100\%}$-$S_{100\%}$		$C_{100\%}$-$S_{50\%}$	
	CDL[a]	CC[b]	CDL	CC	CDL	CC
Co	0.25	6.89	0.011	<1	0.002	3.28
As	0.86	<1	0.523	<1	0.450	<1
Se	0.52	<1	0.235	<1	0.210	<1
Mo	0.72	<1	0.080	<1	0.027	<1
Cd	0.65	<1	2.061	<1	0.121	<1
Sn	0.53	<1	2.075	<1	0.900	<1
Hg	0.30	<1	0.242	<1	0.319	<1

[a] Concentration in the limit of detection
[b] Concentration in leachates
[c] Concentration below the concentration in the limit of detection

8.3.3 Concentrations of Chlorides and Sulfates

Sulfates and chlorides concentrations could not be measured for the leaching series which included the addition of a few drops of HNO_3 during the leaching test (e.g. experimental series L1). The addition of acid during the test increased the concentration of NO_3^- to such concentrations whose peaks were hidden the chlorides and sulfates peaks in the chromatogram.

8.3.3.1 Series L2

Figure 8.13 shows cumulative and relative concentrations of chlorides and sulfates for leaching series L2. Leachates were obtained from mortar specimens containing 15% and 50% of MSWI-BA as replacement of cement and sand respectively and initially cured for 28 and 90 days. Acidic de-ionised water (pH =2) was used as leachant.

- Cumulative concentrations

It is observed that pH(28) curing period exhibited higher leachability of chlorides than the pH(90) curing period. Contrarily, leachates of pH(90) specimens gave higher CC of sulfates than those for pH(28) specimens. That suggested that extended initial curing tends to fix chlorides may be as a result of the formation of chloro-aluminate compounds. However, the high release of sulfates for long initial curing (90 days) can be attributed to the carbonation of ettringite in specimens.

- Relative concentrations

RC of chlorides showed different trend for both curing periods. Thus, pH(28) leachates presented a significant decrease in concentrations of chlorides from 24h to 72h, whereas in pH(90) leachates, the RC of chlorides exhibited a gradual increase in

during the whole test period. The trend of RC of sulfates was similar for both curing period with exception during the leaching period between 168h and 336h.

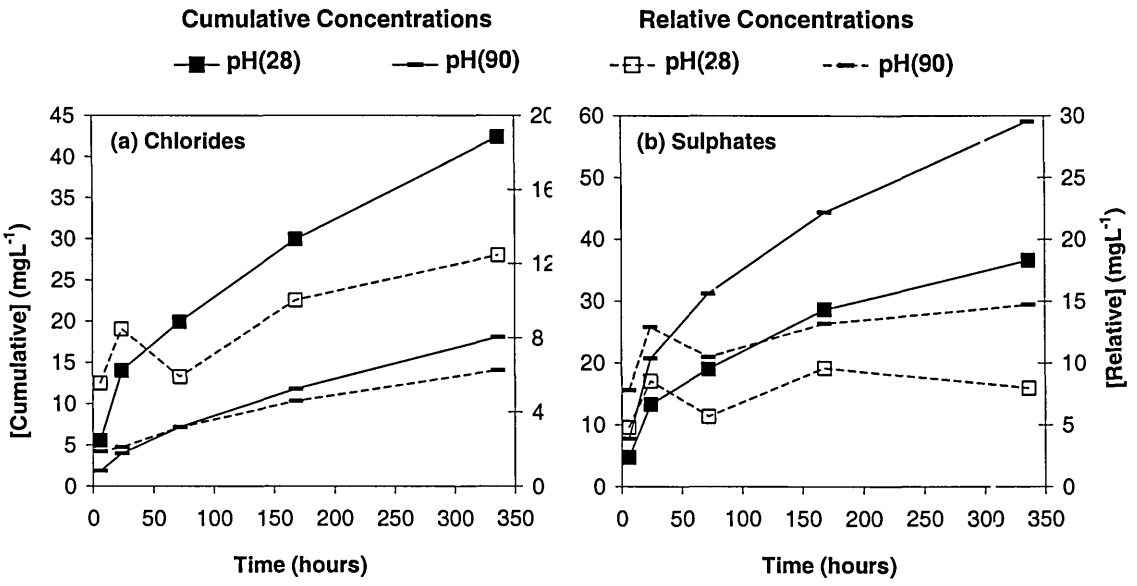


Figure 8.13. Cumulative and relative concentrations chlorides and sulfates in leachates for mortar containing MSWI-BA leached out with and without addition of acid during the test (series L2)

8.3.3.2 Series L3

Figure 8.14 shows cumulative and relative concentrations of chlorides and sulfates in leachates for mortar containing MSWI-BA and initially cured for 28 days. Series L3 included the use of three types of leachants; rain water, deionised water and acidic de-ionised waters (pH =2).

- Cumulative concentrations

Cumulative concentrations of chlorides were similar for pH(28) and Rain(28) leachates and they were higher than in Ion(28) leachates. At the end of leaching test, the difference in Cl^{1-} concentrations was $10mgL^{-1}$ approximately between the different leachates. CC of SO_4^{2-} were significantly higher in pH(28) leachates than in Rain(28) and Ion(28). At the end of the test, SO_4^{2-} concentrations were approximately $35mgL^{-1}$ and $10mgL^{-1}$ for pH(28) and Ion(28) leachates respectively. The concentrations of sulfate in Rain(28) leachates were lower than $1mgL^{1-}$.

- Relative concentrations (RC)

For the three leachants of this experimental series, RC of chlorides showed similar trend. RC showed an increase from 6h to 24h, followed by a significant decrease in concentrations from 24h to 72h. After 72h, relative concentrations of chlorides increased until the end of leaching test.

Trend of RC of sulfates was different in pH(28) and Ion(28) leachates. In pH(28) leachates, RC of SO_4^{2-} increased from 6h to 24h and then decreased significantly from 24h to 72h. After 72h, RC increased again until 168h and decreased from 168h to the end of leaching test. In Ion(28) leachates, RC of SO_4^{2-} showed a continuous decrease from 6h to 72h followed by a significant increase up to 168h and slight decrease until the end of leaching test.

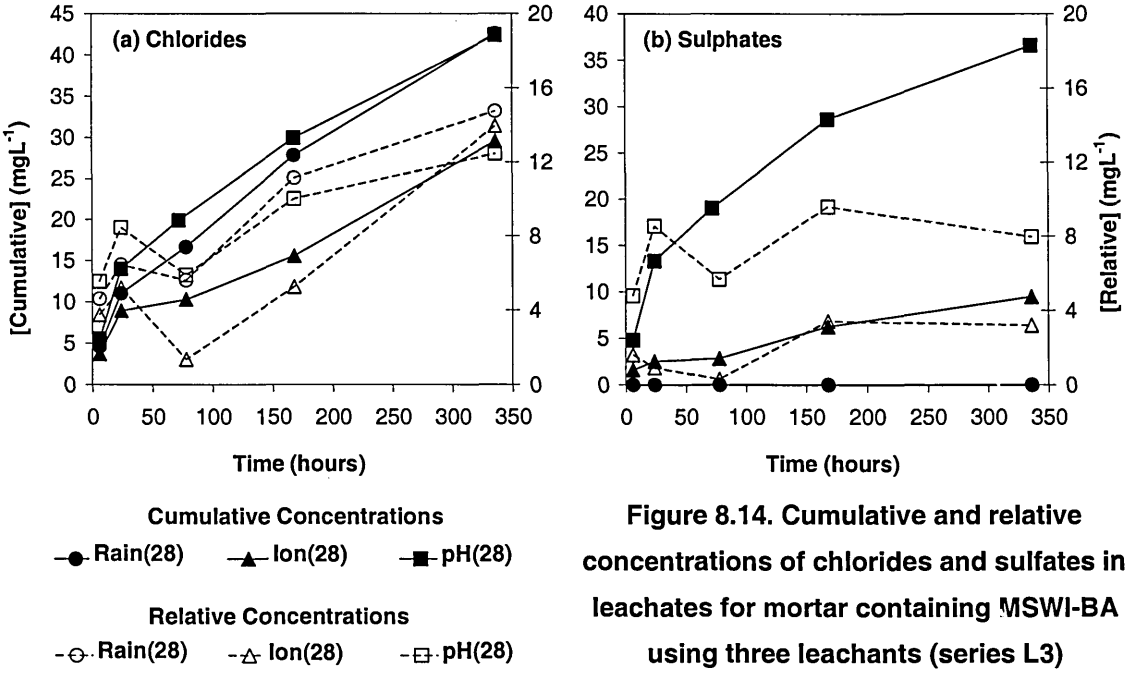


Figure 8.14. Cumulative and relative concentrations of chlorides and sulfates in leachates for mortar containing MSWI-BA using three leachants (series L3)

8.3.3.3 Series L4

Figure 8.15 shows cumulative and relative concentrations of chlorides and sulfates in leachates in leachates from three mixes with different MSWI-BA replacement. The three different mixes were; a mix contained 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively ($C_{85\%}$-$S_{50\%}$); second mix contained 50% of MSWI-BA as relative replacement of sand ($C_{100\%}$-$S_{50\%}$) and the third mix consisted of the reference mix that contained with 100% of cement and sand ($C_{100\%}$-$S_{100\%}$). All mixes were cured for 28 days before the test started.

- Cumulative concentrations

Leachates from specimens containing 15% and 50% of MSWI-BA as replacement of cement and sand exhibited higher concentrations of Cl^{1-} and SO_4^{2-} than those from specimens containing 50% of MSWI-BA as replacement of sand, $C_{100\%}$-$S_{50\%}$. In addition, $C_{100\%}$-$S_{50\%}$ specimens gave higher release of Cl^{1-} and SO_4^{2-} than the reference mix specimens. These results indicated that mix containing MSWI-BA as partial replacement of cement and sand released more chlorides and sulfates than the mix containing MSWI-BA as partial replacement of sand and the control mix.

- Relative concentrations (RC)

Trend of relative concentrations of Cl^{1-} in $C_{100\%}$-$S_{50\%}$ leachates was similar to that in $C_{85\%}$-$S_{50\%}$ leachates, which has been explained in previous series. RC of SO_4^{2-} exhibited a continuous increase in concentration with leaching period in $C_{100\%}$-$S_{50\%}$ and $C_{100\%}$-$S_{100\%}$ leachates.

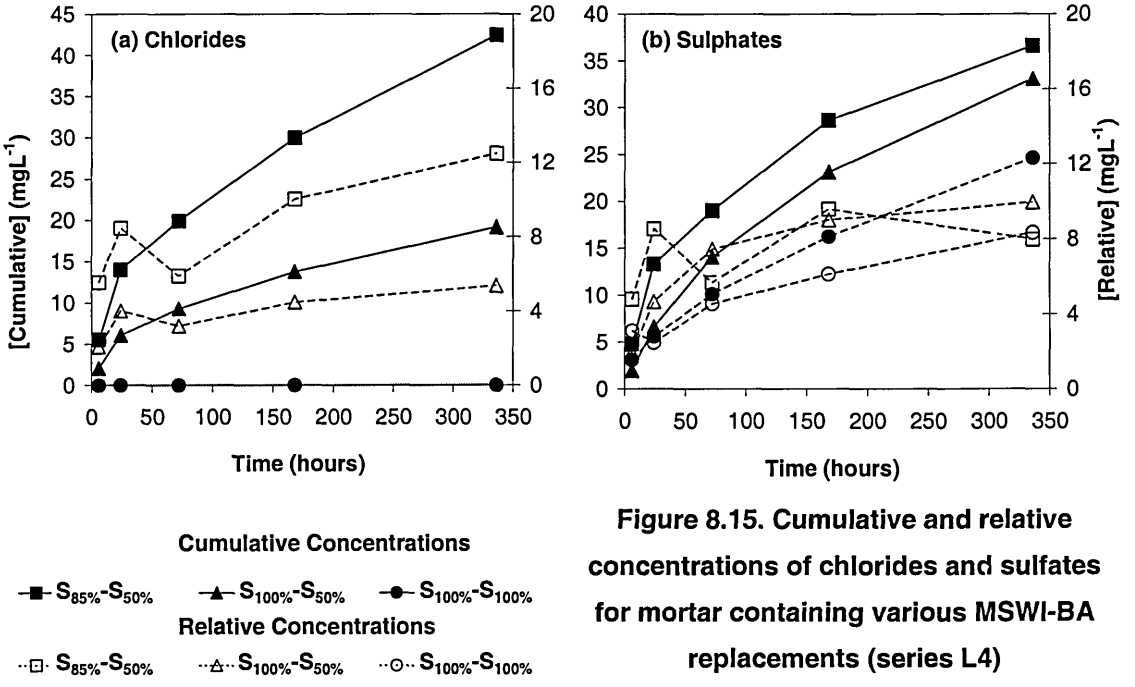


Figure 8.15. Cumulative and relative concentrations of chlorides and sulfates for mortar containing various MSWI-BA replacements (series L4)

8.3.4 Effect of Initial Curing on Extraction of Elements

Table 8.13 summaries the effect of using different initial curing periods on the leachability of mortar specimens containing 15% and 50 % of MSWI-BA as partial replacement of cement and sand respectively.

Extractions of K, Na, Mo, As, Hg, Ni and Cl^- from mortar specimens cured for different initial periods were clearly higher as initial curing period decreased (i.e. 1 day) whereas Si, Al, Mg, Co, Cu, Zn, Pb and SO_4^{2-} concentrations were high in leachates from specimens with initial curing of 90 days. Contrarily, initial curing of specimens did not have significant influence on extractions of Ca, Fe, Cr, Cd, Mn, Ba, Mg, Se, Sn and B.

The higher concentrations of Si, Al, Mg, Co, Cu, Zn, Pb and SO_4^{2-} in leachates from specimens cured for 90 days compared with those cured for 1 day were not expected. This may correspond to the lower sulfate resistance observed for specimens cured initially for 90 days compared with those cured for 2 days (Chapter 7). The increase in leachability of Al and SO_4^{2-} may be attributed the higher carbonation of ettringite of specimens cured initially for 90 days. Carbonation of ettringite provokes the release of Al and SO_4^{2-}. The release of Si, Mg, Co, Cu, Zn and Pb may be associated with

destabilisation of ettringite and/or C-S-H, where these elements could be adhered, as consequence of the decrease in pH caused by carbonation and loss of CH.

The possible formation of a carbonated layer in specimens cured for 1 days and the lack of this layer in those cured for 90 days may also justify the difference in leaching. Osborne (**13**) found for Portland and blast-furnace slag cement concrete that a period of air storage before immersion in sulfate solutions is beneficial to sulfate resistance. Even one day concrete specimens placed in sulfate solution after a few hours exposure to air, showed better resistance to attack than specimens water-cured for up to 28 days. This beneficial effect is thought to be primarily due to the formation of a carbonated outer layer leading to blocking of the pores and refinement of the pore structure.

Table 8.13. Effect of initial curing on leachates concentrations

Element/s	Leachability order	Effect of Initial Curing
Ca, Fe, Cr, Cd, Mn, Ba	90days=1day	No effect
Si, Al, Mg, Co, Cu, Zn, Pb	90days>1day	CC[1] increase as increase curing
Mg, Se, Sn	90dasy≥1day	CC slight increase as increase curing
K, Na, Mo, As, Hg, Ni	1day>90day	CC increase as decrease curing
B	1day≥90days	CC slight increase as decrease curing
Cl^-	28days>90days	CC increase as decrease curing
SO_4^{2-}	90days>28days	CC increase as increase curing

[1] CC concentration

8.3.5 Effect of pH Leachant on Extraction of Elements

Table 8.14 summarises the Influence of leachant pH on leachability of elements examined.

The leachate concentrations for most elements examined (Ca, Si, Mg, Fe, B, Cr, Co, Mn, Ba, Ni, Cu, Zn, Pb, Al, Cd, Se, Mo, Sn, As and Hg) were appreciably dependent on the leachant pH or the pH during the leaching period as it was expected. The concentrations of these elements were higher as pH decreased. In particular concentrations of Al, Cd, Se, Mo, Sn, As and Hg in leachates increased significantly at pH ranging from 2 to 4 (low pH range), whereas concentrations of Ca, Si, Mg, Fe, B, Cr, Co, Mn, Ba, Ni, Cu, Zn and Pb increased significantly at any small variation of pH including pH ranges varying from 2 to 10. These suggested that the first group of elements were in such forms of which were only soluble at low pH, whereas the second group of elements did not need low pH to pass to the leachates. Each element of both groups can be in extensive number of chemical species combined with other elements

presented in the cement-based systems. To suggest the most common chemical forms of each element based only on its solubility at different pH ranges is not possible.

Na and K exhibited similar leaching behaviour under different pH ranges. Thus, their extractions were higher at pH ranging from 4-7 than pH ranges of 2-4 or 7-12 (leachants consisted of de-ionised water or rain water). The pH did not have any effect on the SO_4^{2-} and Cl^- concentrations.

Table 8.14. Effect of pH on leachates concentrations

Elements	PH effect
Ca, Si, Mg, Fe, B, Cr, Co, Mn, Ba, Ni, Cu, Zn, Pb	Significant increase in leaching as pH decrease at all pH ranges examined[1]
Al, Cd, Se, Mo, Sn, As, Hg	Significant increase in leaching as pH decrease at low pH range[2]
K, Na	Slight increase in leaching as pH decrease at high pH range[3]
Cl^-, SO_4^{2-}	No clear influence

1 All pH range included the pH ranges used in leaching series 2 and 3.
2 Low pH range represents the pH of leachants used in leaching series L2 (i.e. acidic de-ionised water and acid de-ionised water with addition of acid to keep the pH between 2 and 4.
3 High pH range represents the pH of leachants used in leaching series L3 (i.e. de-ionised water, rain water and acidic de-ionised without addition of acid).

8.3.6 Effect of type of MSWI-BA Replacement on Extraction of Elements

Table 8.15 summarises the effect of replacing cement and sand with MSWI-BA on leachate concentrations for the different elements examined.

Table 8.15. Effect of type of MSWI-BA replacement on leachates concentrations

Element/s	Leachability Order
Ca,	$C_{100\%}$-$S_{100\%}$>$C_{85\%}$-$S_{50\%}$>$C_{100\%}$-$S_{50\%}$
Si,	$C_{100\%}$-$S_{100\%}$=$C_{100\%}$-$S_{50\%}$>$C_{85\%}$-$S_{50\%}$
Al, Mg, Fe, K, Na, Mn, Ba, Pb, Co, Cl^-, SO_4^{2-}	$C_{85\%}$-$S_{50\%}$>$C_{10U\%}$-$S_{50\%}$>$C_{100\%}$-$S_{100\%}$
Ni	$C_{85\%}$-$S_{50\%}$≅$C_{100\%}$-$S_{50\%}$>$C_{100\%}$-$S_{100\%}$
Cu	$C_{85\%}$-$S_{50\%}$>$C_{100\%}$-$S_{50\%}$≅$C_{100\%}$-$S_{100\%}$
Cr	$C_{100\%}$-$S_{100\%}$>$C_{100\%}$-$S_{50\%}$≅$C_{85\%}$-$S_{50\%}$
B, Zn,	No clear influence

Replacing 15% cement with MSWI-BA (∅<212μm) and 50% sand with MSWI-BA (212μm<∅<2.36mm) caused a regular increase in the leachate concentrations for Al, Mg, Fe, K, Na, Mn, Ba, Pb, Co, SO_4^{2-} and Cl^- compared with the concentrations observed in leachates from specimens made with 100% cement and class M sand, the reference mix. Replacing sand with 50% of MSWI-BA regardless of replacing cement effect, increased the Ni concentrations compared the reference mix leachates. Replacing cement with 15% of MSWI-BA regardless of replacing sand effect, increased the Cu concentrations compared the reference mix leachates.

In addition, replacing cement with MSWI-BA reduced leachate concentrations for Ca and Si compared with leachates from the reference mix specimens. Concentration of Cr was lower in leachates from specimens containing MSWI-BA than those for the reference mix.

8.3.7 Comparison of Leaching Behaviour between Unbound and Bound MSWI-BA

The efficiency of cement-based systems to immobilise elements from the fractions of MSWI-BA examined (∅<212μm and 212μm<∅<2.36mm) is evaluated here. In Chapter 5 was shown the concentrations in leachates from unbound fractions of MSW-BA ∅<212μm and 212μm<∅<2.36mm that were leached out separately using NEN 7341 test method. In Chapter 8 is presented the concentrations in leachates from mortar specimens that contained different replacement of MSWI-BA. Mortars examined had different constituents. One mix contained 15% and 50% of MSWI-BA (∅<212μm and 212μm<∅<2.36mm) as partial replacement of cement and sand respectively, symbolised $C_{85\%}$-$S_{50\%}$. Other mix contained 50% of MSWI-BA (212μm<∅<2.36mm) as partial replacement of sand mix, $C_{100\%}$-$S_{50\%}$. The third mix consisted of the reference mix, $S_{100\%}$-$S_{100\%}$. A broad estimate of the extracted amounts of some elements from each of the bound fractions of MSWI-BA has been made by subtracting the extraction amounts from the specimens of the reference mix.

Table 8.16 shows the extractions of some elements per kg of MSWI-BA from the unbound and bound fractions MSWI-BA with 212μm<∅<2.36mm and ∅<212μm.

In general, it was found that the leachability of the fraction of MSWI-BA (212μm<∅<2.36mm) used as partial replacement of sand was significantly reduced when it was bound. The leachability of fraction of MSWI-BA used as a partial replacement of cement was also reduced, but less than the leachability of the coarse fraction. This high reduction of leachability of bound MSWI-BA suggests that the use of the both fractions examined as construction materials can be possible without causing any risk to the environment.

Table 8.16. Comparison of leachability between unbound and bound MSWI-BA

Elements	Concentration in Leachate (mg/kg MSWI-BA)				Unbound/bound ratio	
	Unbound		Bound			
	Coarse[1]	Fine[2]	Coarse	Fine	Coarse	Fine
Al	8996	65478	29.95	189	300	347
Mg	3710	2697	7.86	120	472	22
K	2521	2597	189	2249	13	1
Na	3814	3631	356	2480	11	1.5
Fe	6843	589	3.09	25.68	2213	23
Mn	179	213	0.56	4.46	321	48
Co	6.10	7.00	0.03	0.32	209	22
Ni	22.63	23.65	0.05	0.15	481	162
Cu	255	679	1.81	35.80	141	19
Zn	1538	1270	17.17	-	90	-
Ba	83.40	139.43	1.21	19.44	69	7
Pb	278	919	1.22	9.90	228	93

1-Coarse fraction of MSWI-BA 212μm<Ø<2.36mm

2-Fine fraction of MSWI-BA Ø<212μm

Concentrations of As, Se, Mo Cd and Sn in leachates from specimens containing MSWI-BA either as partial replacement of sand or cement and sand were below 1μg/l. This indicated that when MSWI-BA was bound in cement-based systems the leachability of these elements was very low and similar to detection limit concentrations. In addition, concentrations of Ca, Si, B and Cr in leachates from specimens containing MSWI-BA either as partial replacement of sand or cement and sand were lower than those for the reference mix. This suggested that the cement-based systems containing MSWI-BA immobilised better Ca, Si, B and Cr than the reference systems made with cement and natural aggregates. The lower leaching release of Ca in mortars made with MSWI-BA compared with the reference specimen may indicate the consumption of Ca from the hydration of cement to form C-S-H (pozzolanic reaction).

8.4 CONCLUSIONS

This chapter has evaluated the leaching behaviour of mortar specimens considering two aspects; firstly, leachability of mortar containing 15% of MSWI-BA as a partial replacement of cement and 50% of MSWI-BA as a partial replacement of sand has been investigated under various experimental leaching parameters such as different initial curing periods; pH and various leachants. Secondly, the influence of replacing cement or sand or both on the leachability has been examined. Leachability has been evaluated by determining the concentrations of Ca, Si, Mg, Fe, Na, K, B, Cr, Co, Mn, Ba, Ni, Cu, Zn, Pb, Al, Cd, Se, Mo, Sn, As, Hg, and Cl^- and SO_4^{2-} in leachates.

The effect of initial curing period on leachate concentrations was not the same for all the elements examined. The four different trends observed are as follows:

- Higher leachability at short initial curing periods (K, Na, As, Mo, Hg, Ni and Cl^-)
- Higher leachability at long initial curing periods (Si, Al, Mg, Co, Cu, Zn, Pb and SO_4^{2-})
- Initial curing period did not have any effect on leachability (Ca, Fe, Cr, Mn, Ba and Cd)
- Initial curing period did not have a significant influence on leachability (Mg, Se, Sn, and B)

These differences in leaching behaviour for the elements examined may be attributed to the formation of distinct phases for each element along the curing periods.

In general as it was expected the leachate concentrations for most elements examined (Ca, Si, Mg, Fe, B, Cr, Co, Mn, Ba, Ni, Cu, Zn, Pb, Al, Cd, Se, Mo, Sn, As and Hg) were appreciably dependent on the leachant pH or the pH during leaching. On the other hand, pH did not have any effect on the SO_4^{2-} and Cl^- concentrations.

Leachate concentrations from mortar specimens containing 15% and 50% of cement and sand with MSWI-BA caused an increase in concentrations for Al, Mg, Fe, K and Na compared with those the reference mix specimens. However, concentration of Ca, Si and Cr were higher in leachates from specimens containing 100% cement and class M sand than for those containing MSWI-BA as partial replacement of cement and sand.

Finally, the comparison of leaching behaviour of the bound and unbound fraction of MSWI-BA examined has indicated the high efficiency of cement-based systems to immobilise elements such as Co, Ni and Pb and also suggested that the use of both fractions as construction materials is possible from the environmental view point.

8.5 REFERENCES

1 Johnson C.A., Kersten M., Ziegler F. and Moor C. "Leaching Behaviour and Solubility Controlling Solid Phases of Heavy Metal in Municipal Solid Waste Incinerator Ash". Waste Management. Vol.16, Nos. 1-3 , pp 129-134.1996

2 Sanchez F., Barna R., Garrabrants A. Kosson D.S and Moszkowicz P. " Environmental Assessment of a Cement-Based Solidified Soil Contamited with Lead". Chemical Engineering Science Vol 55 pp 113-128. 2000

3 Stegemann J.A., Cote P.L. "A Proposed Protocol for Evaluation of Solidified Wastes". The Science of the Total Environment Vol. 178 pp 103-110. 1996.

4 Andac M. Glasser F.P. "Effect of Test Conditions on the Leaching of Stabilised MSWI-Fly ash in Portland Cement". Waste Management, Vol. 18, pp 309-319. 1998.

5 Alucha. "Leaching Standard For Quality Control of Aggregates". Waste Materials in construction. Woolley G.R., Goumans J.J.J.M. and Wainwright P.J. Elsevier Science. 2000

6 Groot G.J., I., Hohberg F.J., A.M.H. Lamers, Van Der Veen, Wassing W. and Quevauviller P.H. "Development of Leaching Method for the Determination of Environmental quality of Concrete". European Commission. BCR Information . 1997.

7 NEN 7345 03. 95.: Leaching Characteristics of Solid Earthy and Stony Building and Waste materials. Determination of the Leaching behaviour of Inorganic Components from Building Monolithic Waste Materials with the Diffusion Test

8 Quenee B., Li G., Siwak J.M. and Basuyau V. "The Use of MSWI Bottom Ash as Aggregates in Hydraulic Concrete". Waste Materials in construction. Woolley G.R., Goumans J.J.J.M. and Wainwright P.J. Elsevier Science. 2000

9 Polettini A., Polettini S., Pomi R. and Sirini P. "Physical Properties and Acid Neutralisation Capacity of Incinerator Bottom Ash-Portland Cement Mixtures". Waste Materials in construction. Woolley G.R., Goumans J.J.J.M. and Wainwright P.J. Elsevier Science. 2000

10 BS 12. 1996: Specification for Portland cement.

11 BS 882:1992. Specifications for Aggregates from Natural Sources for Concrete.

12 EPA. Toxicity Characteristic Leaching Procedure Method 1311. July 1992.

13 Osborne G.J. "Durability of Portland Blast-Furnace Slag Cement Concrete". Cement and Concrete Composites. Vol. 21, pp 11-21. 1999

CHAPTER 9: CONCLUSIONS, LIMITATIONS AND FUTURE RECOMMENDATIONS

9.1 CONCLUSIONS

This research programme has investigated the physical, mechanical, sulfate resistance properties and leaching behaviour of MSWI-BA with particle size diameter below 2.36mm to find its potential uses in construction. This fraction of MSWI-BA is currently rejected for further uses due to its poor engineering properties and, therefore, it is disposed of in landfill sites.

MSWI-BA fraction with ∅<2.36mm was divided into two fractions, fine (∅<212μm) and coarse (212μm<∅<2.36mm) fractions, which have been used as partial replacement of cement and sand respectively. The selection of these fractions was based on the higher compressive strengths compared to other fractions when they were contained in mortars. Mortars containing 25% of fine fraction of MSWI-BA showed slightly higher strength than mortar containing inert silica at the same cement replacement level. This suggested a possible pozzolanic activity of the fine fraction of MSWI-BA. Other properties particularly compaction have a significant positive effect on strength of systems containing waste or recovered materials. Moreover, the compressive strength of mixes containing 25% or 50% of the coarse fraction of MSWI-BA as a partial replacement of sand were similar or exceeded those of the reference mix.

- **Physical and chemical properties of unbound MSWI-BA**

The examination of particle and bulk densities, particle size distribution, pH, inorganic composition and LOI of the fine and coarse fractions of MSWI-BA has shown that:

1. The fine fraction exhibited lower particle and bulk densities and higher Cl and SO_3 contents than cement. However, the content of the main elements (i.e. Si, Ca, Al), which are involved in the formation of calcium silicate hydrates, are similar to those for slag and fly ash.
2. The properties of the coarse fraction indicated that this fraction can be used as aggregate, however its content of SiO_2 and CaO were lower and higher respectively than those for class M sand. This fraction also exhibited lower particle and bulk densities than Class M sand.

- **Leaching behaviour of unbound fine and coarse fractions**

Concentrations in leachates from the unbound fractions were determined using NEN 7341 procedure (2 stages, first pH=7 and second pH=4, duration 3 hours each) and TCLP (initial pH=2.88, duration 24 hours) procedure. The analysis of leachate concentration indicated:

3. For both fractions of MSWI-BA, three groups of elements were found in descending concentrations. The first group contained major elements which involved Ca, Si,

Na, K, Al, Fe, Mg and Zn; the second group contained minor elements (i.e. Pb, Cu, Mn and Ba); the third group contained trace elements (i.e. B, Ni, Cd, Co, Cr, Mo, Se, As, Sn and Hg). The concentration of each element was dependent upon the MSWI-BA fraction examined and the leaching procedures carried out.

4. Fine fraction of MSWI-BA exhibited higher concentrations of Ca, Cr, and As than the coarse fraction, whereas the coarse fraction had higher concentrations of Si, Al and Fe. Concentrations of Mg, Mn, Ni, Cd, Co, Sn and Mo did not differ substantially between both fractions. Concentrations of Na, K, Zn, Cu, Ba, B, Se and Hg did not show a clear trend in both fractions. They were dependant upon the leaching procedure carried out.
5. Concentrations of most elements in leachates, obtained using the NEN 7341 procedure, exhibited higher concentrations than those using TCLP, regardless of the MSWI-BA fraction examined. The difference in concentrations between both leaching procedures was high for Si, Fe, Mn, Ba, Pb, Co, Ni, Cu, Zn and Al. This suggested that these elements dissolved as cationic forms, which are more soluble in acid conditions and strongly pH dependant.
6. Examination of the concentrations in leachates obtained at pH=7 or pH=4 stage of the NEN 7341 leaching procedure indicated that the extractions of Si, Mg, Al, Fe, Mn, Cu, Zn Pb Cr, Ni, As, Se, Cd was dependant upon the fraction of MSWI-BA examined. This can be attributed to the difference in particle size, element content and phases associated with these elements between both fractions. In contrast, Ca, Na, K, Ba, B, Co, Mo, Sn and Hg exhibited similar pH effect in both.
7. Grinding both fractions of MSWI-BA to the same particle size increased their leachability significantly.
8. Concentrations of Ni, Cu, Zn, Cd and Pb in leachates from the ground fraction, which had initially a particle size with ∅<2.36mm, exceeded slightly the tolerable limits for soils or mineral waste used within the European Union. This suggested that stabilisation with cementitious materials is possible when disposed of in landfill sites.

- **Mechanical, physical and sulfate resistance of mortar containing MSWI-BA**

The evaluation of replacing cement and sand on mechanical, physical and sulfate resistance properties of mortars containing various replacement levels of the fine and coarse fractions of MSWI-BA has found that:

9. There was a higher reduction in compressive strength when 50% of sand was replaced compared to a 25 % replacement level at the same cement replacement levels.

10. The saturated density decreased as cement and sand replacement levels increased.
11. The drying shrinkage increased as cement replacement levels increased. The increase in sand replacement level from 25% to 50% has less influence than the increase in cement replacement level.
12. Flexural and equivalent cube strengths decreased as cement replacement levels increased. However, there was a small difference in flexural and equivalent cube strengths as a result of using either 25% or 50% sand replacement level.
13. Total pore volume (TPV) increased as cement and sand replacement levels increased. However, the TPV of the mix containing 15% of the fine fraction was similar to the reference mix. The TPV of all the mixes examined decreased as curing period increased as expected.
14. The percentage of small pores ($\varnothing p<0.1\mu m$) was lower for mixes containing MSWI-BA as partial replacement of cement or sand compared to the reference mix percentage. This suggested that there was not a refinement of the small pores as a result of later formation of calcium silicate hydrates.
15. Sulfate resistance decreased significantly as cement replacement levels increased from 30% to 50%. However, replacing cement with 15% of fine fraction caused a slight reduction in sulfate attack compared to that of the reference mix.
16. The appearance of specimens containing 25% and 50% of the coarse fraction as a partial replacement of sand indicated a higher degree of sulfate attack compared with the reference mix specimens. However, changes in length and strength of these specimens were similar to those of the reference mix. Specimens containing 50% of MSWI-BA as a partial replacement of sand showed slightly higher degree of attack than those containing 25% replacement levels.
17. Replacing cement and sand with MSWI-BA generally increased the degree of sulfate attack as replacement levels increased. However, there are some exceptions. Sulfate resistance of specimens containing 15% of the fine fraction as a partial replacement of cement and either 25% or 50% of the coarse fraction as a partial replacement of sand was similar to that for specimens containing 100% cement in the binders and 25% or 50% sand replacement level.
18. Specimens immersed in $MgSO_4$ solution showed higher deterioration than those in Na_2SO_4 solution regardless of the different initial curing periods examined.
19. Deterioration of specimens exposed to either Na_2SO_4 or $MgSO_4$ solution increased as initial curing period increased. This was not expected. However, further examination of the leaching behaviour for the same mixes indicated the same trend. This may be attributed to the formation of ettringite at the early plastic stage,

which can be accommodated without disrupting the structure. Possible ettringite carbonation of specimens cured for 90 days may also decrease the sulfate resistance compared with specimens cured for short periods. A possible formation of a carbonation layer at the early hydration stage can produce an outer layer that impedes the flow of aggressive solutions (i.e. acidic leachants or sulfate solutions) through mortar specimens.

20. C_3A content of cement had a different influence on sulfate resistance depending on the type of exposure used. In $MgSO_4$ immersion, specimens made with cement with low (7.1) and high (11.2) C_3A contents exhibited similar deterioration rate and degree of attack. This indicated that in $MgSO_4$ exposure, in addition to the attack on C_3A hydrated products (C-A-H), where ettringite was formed, other hydrated products involved (i.e. C-S-H) could cause higher deterioration than the formation of ettringite. This was attributed to the formation of gypsum as a result of reaction of C-S-H with $MgSO_4$ from the solution. However, in Na_2SO_4 solution, specimens made with high C_3A cement showed higher deterioration rate and sulfate attack than those made with low C_3A cement. This difference in sulfate attacks can be attributed to high ettringite formation when high C_3A cement was used.

- **The leaching behaviour of mortar containing MSWI-BA**

The effects of the specimen initial curing period, pH during the test and the type of leachant, on the concentrations in leachates from mortar specimens containing 15% and 50% of MSWI-BA as partial replacement of cement and sand respectively were as follows:

21. The effect of initial curing period on extractions obtained was not the same for all the elements examined. The difference in leaching behaviour depending on the initial curing period of specimens may be attributed to the formation of different phases for each element examined throughout the curing of samples.

22. Most elements examined (i.e. Ca, Si, Mg, Fe, B, Cr, Co, Mn, Ba, Ni, Cu, Zn, Pb, Al, Cd, Se, Mo, Sn, As and Hg) were appreciably dependant upon the pH of the leachants or the pH during leaching. In contrast, the pH did not have any influence on the SO_4^{2-} and Cl^- concentrations.

23. Concentrations of Al, Mg, Fe, K and Na were higher in leachates from mortar specimens containing 15% and 50% of the fine and coarse fractions of MSWI-BA as replacement of cement and sand than those from the reference specimens. However, concentration of Ca, Si and Cr were higher in leachates from specimens of the reference mix than for those containing MSWI-BA as partial replacement of cement and sand.

24. The comparison of leaching behaviour of the bound and unbound fractions of MSWI-BA with $\varnothing$<212μm and 212μm<$\varnothing$<2.36mm indicated the high efficiency of the cement-based system to immobilise elements (i.e. Co, Ni and Pb) of both fractions of MSWI-BA examined especially for the coarse fraction. Hence, the use of MSWI-BA with $\varnothing$<212μm and 212μm<$\varnothing$<2.36mm as construction materials does not, under the conditions investigated , pose any risk to the environment.

9.2 LIMITATIONS

The limitations of the research programme are the follows:

1. The majority of the findings from this investigation, especially those related to the utilisation of the fine fractions of MSWI-BA ($\varnothing$<212μm) as a partial replacement of cement, could not be compared with other results because of the lack of published work in this area. However, attempts have been made to compare this fraction with cement and well-know wastes (i.e. slag and fly ash).
2. High fineness and low particle size diameters of pozzolanic materials increase the pozzolanic reactivity. However, the fine fraction of MSWI-BA used in this investigation was coarser than the mean particle diameters of other cementitious or pozzolanic materials (i.e. 35-75μm).
3. The use of other tests including X-Ray diffraction and/or scanning electron microscopy analysis would have resulted in better interpretations of data in this research programme.
4. The pH of the leachates during the tank leaching procedure was only recorded each time the leachant was removed. However, continuous monitoring of the pH throughout the test will contribute towards the explanations of the concentrations in leachates.
5. Porosity and pore size distribution of mortar was measured using intrusion porosimetry which has certain limitations. The intrusion of mercury under pressure can damage the pore structure of mortar samples and therefore the pore size distribution may be affected. However, the total pore volume should not be affected.
6. Attempts have been made to compare leaching behaviour of bound and unbound MSWI-BA. However, these comparisons were based on two different leaching procedures.
7. There is a great variation in the chemical and physical properties of MSWI-BA, even for the same incineration facility. During the current research the MSWI-BA was collected from the same incineration plant.

8. Carbonation of specimens exposed to sulfate solutions and leaching may affect the sulfate resistance and leaching behaviour of mortar specimens. However, no carbonation test was conducted to observe the possible relationship between these parameters.

9.3 FUTURE RECOMMENDATIONS

There is a need to use MSWI-BA due to the large quantities generated and the scarcity of landfill sites. The present investigation has shown that there is potential use of MSWI-BA as a partial replacement of cement or sand to produce pre-cast concrete units such as paviers, slabs and blocks. The recommendations for understanding the MSWI-BA behaviour in cement-based systems and therefore enhancing its future use are to:

1. One of the major factor that determine the potential use of MSWI-BA in cement and concrete is its initial processing (combustion temperatures, combustions period, quenching, storage) as this determines its phase composition. Future work using MSWI-BA should consider to collect the MSW-BA before the quenching tank and to improve the combustion (temperature and period) to enhance the MSWI-BA properties.
2. Evaluate the improvement in strength of mortar and concrete as a consequence of grinding the fraction of MSWI-BA when used as a partial replacement of cement.
3. Carry out X-Ray diffraction and scanning electron microscopy to facilitate the interpretation of results on strength, leaching and sulfate resistance.
4. Monitor the pH continuously throughout the leaching test.
5. Carry out testing on MSWI-BA from different incineration facilities.
6. Conduct carbonation test to evaluate the effect on leaching and sulfate resistance.
7. Produce trial industrial concrete products containing MSWI-BA to compare compliance criteria with existing concrete products.

APPENDIX

APPENDIX A

Fe				
Mass	54	56	57	58
Abun. %	5.8	91.72	2.2	0.28
Cr	2.37			
Ni				68.10
ArO	0.06	99.36	0.04	0.20
KO		0.05	6.90	
CaO		96.71	0.04	0.84
AlAl	100			
SiSi		85.06	8.61	5.94
Pd	26.49			
Cd+2	0.90	24.13	28.73	7.50
Sn+2		0.97	0.65	14.53
CrH	9.50			
MnH		99.98	0.02	
FeH			91.71	2.21
NAr	99.24			
OAr	0.06	99.36	0.04	0.20
FAr			0.06	
NeAr		0.31		0.09
FCl	75.77	24.23		
NeCl		0.21	28.93	0.07
NaCl				75.77

B		
Mass	10	11
Abun. %	19.9	80.1
BH		19.9

Ni					
Mass	58	60	61	62	64
Abun. %	68.08	26.2	1.14	3.63	0.93
Fe	0.28				
Zn					48.6
ArO	0.199				
CaO	0.839	2.08			0.19
ScO			99.76	0.04	
TiO				7.98	73.64
SiSi	5.94	0.1			
PP				100	
SS					90.29
Cd+2	7.49				
Sn+2	14.53	32.6	4.63	5.79	
FeH	2.21				
CoH		100	0.015		
NiH		0.01	26.22	1.14	
CuH					69.16
OAr	0.2				
NaAr			0.63		
MgAr		0.27	0.34	0.09	78.68
SiAr					0.31
NaCl	75.77	24.2			
MgCl		7.58	27.48	2.42	
AlCl				75.77	24.23
SiCl					3.54

Cu		
Mass	63	65
Abun. %	69.17	30.83
ScO	0.20	
TiO	7.29	5.53
SS		1.42
Ba+2		0.10
NiH	3.63	0.93
CuH		0.01
ZnH		48.59
NaAr	99.60	
MgAr		9.96
AlAr	0.34	0.06
SiAr		0.02
MgCl	2.67	
SiCl	69.88	24.69

Ba		
Mass	137	138
Abun. %	11.23	71.7
SnO		4.68
SbO	57.22	0.22
ZnZn	0.5	0.23
BaH	7.85	11.23
MoAr	9.51	24.04
MoCl	2.33	
RhCl		75.77
PbCl	0.77	

Cr				
Mass	50	52	53	54
Abun. %	4.34	83.79	9.50	2.36
Fe				5.80
SO	4.39	0.03		
ClO		0.03	24.32	
ArO		0.34		
MgMg	18.39	1.2		
AlAl				100
Mo+2	9.63			
Pd+2		11.15	27.36	26.49
Cd+2			1.25	0.89
CrH			83.78	9.50
CAr	0.06	98.5	1.10	
BAr	19.82			
NAr	0.34	0.06		99.24
OAr		0.34		0.06
CCl	0.28			
NCl	0.28	0.09		
Ocl		0.03	24.32	
FCl				75.77

Rb		
Mass	85	87
Abun. %	72.17	27.8
ZnO	0.01	
RbO		0.01
ScAr	99.6	
CaCl	0.05	
CrCl	3.3	64.5

Mg			
Mass	24	25	26
Abun. %	78.99	10	110.1
LiO	0.05	0.19	
BeO		99.76	0.03
BO			19.85
CC	97.81	2.18	0.01
Ca+2	0.19		
Ti(+2)	73.8	5.4	
V(+2)		0.25	
NaH	99.98	0.01	
MgH		78.98	10.01

In		
Mass	113	115
Abun. %	4.3	95.7
Cd	12.22	
Sn		0.34
MoO	9.56	0.03
FeFe	4.04	0.01
CdH	24.13	28.73
SnH	0.97	0.65
AsH	0.06	99.6
SeH	0.03	
SeCl	20.29	43.35

Mn	
Mass	55
Abun. %	100
KO	93.04
Pd+2	11.73
Cd+2	12.49
CrH	2.36
FeH	5.8
NAr	0.37
FAr	0.34
OCl	0.05

As	
Mass	75
Abun. %	100
CoO	99.76
NiO	0.03
SeH	0.89
ClAr	75.48
KAr	0.31
ArCl	75.78
CaCl	73.45

Co	
Mass	59
Abun. %	100
KO	0.1
CaO	1.14
SiSi	0.29
Sn+2	24.23
FeH	0.28
NiH	68.07
Far	99.6
NaAr	0.34
MgCl	59.85

Al	
Mass	27
Abun. %	100
BO	79.92
Fe+2	5.8
MgH	11.01

Sc	
Mass	45
Abun. %	100
AlO	0.2
SiO	4.7
Zn+2??	51.45
CaH	2.09
BCl	15.08

Se						
Mass	74	76	77	78	80	82
Abun. %	0.84	9.36	7.63	23.78	49.61	8.73
FeO	0.46					
CoO		0.04	0.2			
NiO	67.92	26.3	1.15	3.68	0.9	
CuO					0.26	0.01
ZnO					48.48	27.93
ClCl	5.87					
ArAr		0.67		0.13	99.2	
KK				88.97	12.55	0.45
CaCa					93.98	1.25
AsAr		99.98	0.01			
SeH			9.36	7.63		
SAr	4.1	0.02				
ClAr			24.13			
KAr			0.08		0.01	
CaAr		0.33		0.06	96.56	0.65
ArCl			24.13			
KCl	70.66	27.7		1.63		
CaCl			23.98	0.1	0.03	
ScCl						24.23

Mo							
Mass	92	94	95	96	97	98	100
Abun. %	14.84	9.25	15.92	16.68	9.55	24.13	9.63
AsO	0.04						
SeO	9.34	23.75	0.02	49.54	0.02	8.81	0.02
CrCr							0.19
Hg+2						0.15	23.1
MoH			9.25	15.92	16.68	9.55	
CrAr	83.45	2.36					
MnAr			96.6				
FeAr	0.31	5.84		91.35	2.2	0.28	
CoAr			0.34		0.06		
NiAr		0.23		0.13		67.83	26.12
ZnAr							0.16
MnCl	24.23						
FeCl	1.67	0.53	0.07				
CoCl		75.77		24.23			
NiCl			36.36	0.86	9.11	0.28	
CuCl						52.41	40.12

Sn										
Mass	112	114	115	116	117	118	119	120	122	124
Abun. %	0.97	0.65	0.34	14.53	7.68	24.23	8.59	32.59	4.63	5.79
Cd	24.13	28.73		7.49						
In			95.7							
MoO	16.67	24.11	0.03	9.66		0.02				
CdO									1.25	0.89
FeFe	84.16	0.56	0.01							
CoCo						100				
NiNi				46.35		35.7	1.55	11.82	3.18	0.62
CdH	12.8	12.22	28.73		7.49					
InH		4.3		95.69	0.01					
SnH			0.65	0.34	14.53	7.68	24.23	8.59		
SbH									57.35	42.63
AsAr			99.6							
SeAr	0.03	0.97		9.5	7.6	23.75		49.42	8.69	
AsCl	24.23									
SeCl	5.78	1.85	43.35		16.64		2.11			
RbCl								54.68	38.58	6.74

Zn					
Mass	64	66	67	68	70
Abun. %	48.6	27.9	4.1	18.8	0.6
Ni	0.93				
CaO	0.19				
TiO	73.64	5.54	0.01	0.011	
CrO		4.335		83.6	2.5
FeO					5.79
SS	99.29	8	0.06	0.21	
ClCl					57.4
Ba+2		0.1	2.42	7.85	
CuH	69.16	30.82			
ZnH			27.9	4.1	
MgAr	76.68	10.97			
AlAr			99.6		
SiAr	0.31	0.7		91.86	3.09
PAr			0.34		
SAr				0.32	0.07
AlCl	24.23				
SiCl	3.54	1.13	0.75		
PCl		75.77		24.23	
SCl			72	0.57	0.18
ClCl					57.41

APPENDIX B

The influence of using a contact angle of either 130°C or 141°C on the cumulative pore volume (CPV) and relative pore volumes (RPV) were examined for four samples. These samples consisted of mortar containing 15% of MSWI-BA ($\varnothing$<212μm) as a partial replacement of cement and 50% of MSWI-BA (212μm<$\varnothing$<2.36mm) as a partial replacement of sand. The mortar samples were obtained from the same batch and MIP analysis was carried out at same curing period of 7 days. Figure 1 shows the CPV, expressed in mm^3/g, and RPV, expressed in %, plotted against pore size distribution. For the four samples examined, the CPV and RPV using a contact angle of either 130°C or of 141°C were similar. For sample A and B, there was a slight difference in RPV when the contact angle was different for pore diameters around 0.1 microns.

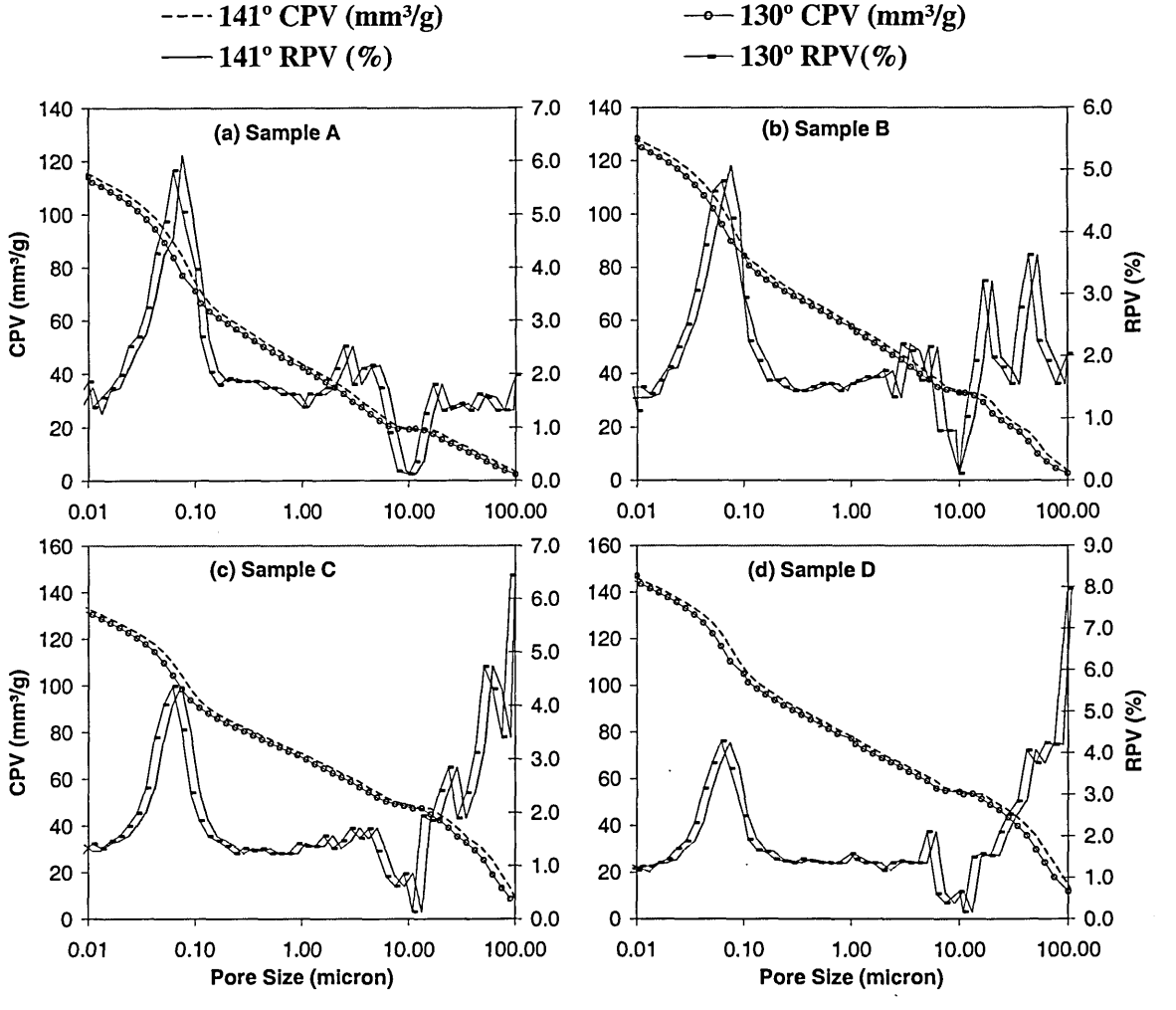


Figure 1. Influence of contact angle on cumulative and relative pore volume (CPV, RPV) for (a) Sample A; (b) Sample B (c) Sample C and (d) Sample D

APPENDIX C

The effect of using either one or two pieces on CPV and TPV was evaluated. The total mass of samples was kept approximately constant for each MIP analysis and the contact angle was of 141º. Figure 2 shows the comparison of CPV and RPV between MIP analysis that were carried out using one piece (e.g. sample A and B) or two pieces (e.g. sample C and D). Results indicated that the samples containing 2 pieces (e.g. sample C and D) exhibited approximately 20mm^3/g more of CPV than samples containing one piece (sample A and B). In addition, for a pore size of 100μm approximately, samples containing 2 pieces gave higher RPV compared with samples containing one piece. Whilst, for pore below 10μm samples containing one piece exhibited higher RPV than those samples containing two pieces.

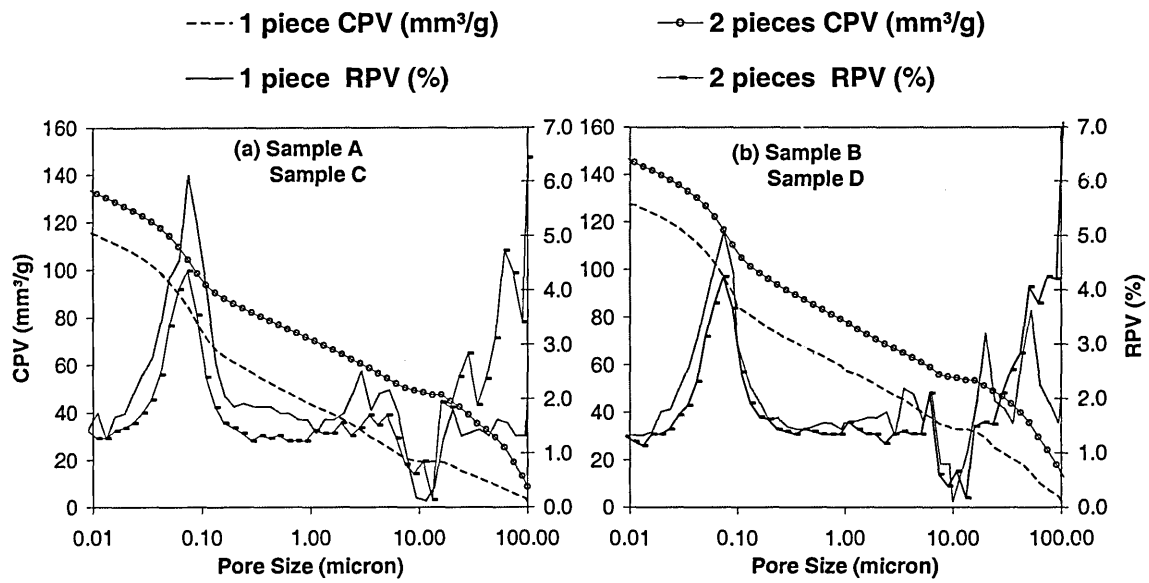


Figure 2. Influence of number of pieces on cumulative and relative pore volumes (TPV and RPV) at 7 days curing.